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ORGANIC COMPOUNDS OF MERCURY

BY

FRANK C. WHITMORE, PH.D.
PROFESSOR OF ORGANIC CHEMISTRY,
NORTHWESTERN UNIVERSITY

American Chemical Society
Monograph Series

BOOK DEPARTMENT

The CHEMICAL CATALOG COMPANY, *Inc.*
ONE MADISON AVENUE, NEW YORK, U. S. A.
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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coordinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coordinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of cooperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped therefore that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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For additional information regarding this series of monographs, see General Introduction, page 3. As the number of copies of any one monograph will be limited, advance orders are solicited.

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AUTHOR'S PREFACE

Organic compounds of mercury have been studied by many investigators from 1850 to the present time. The interest in these substances has increased in recent years because of the need for some non-ionized mercury compound for use with the organic arsenicals in the treatment of syphilis. The total amount of work which has been done on organic mercury compounds is probably greater than that done on the arsenicals but it has received much less publicity. Although a number of monographs have been written in English and in German on the arsenic compounds none has appeared in any language on the mercurials.

Originally the writer hoped to include in the present monograph all of the organic compounds which contain mercury in any form. It soon became evident that the work could not be all-inclusive. Attention will therefore be confined almost entirely to the true organic mercury compounds in which mercury is attached directly to carbon. These substances have practically none of the properties of mercuric salts. The O — Hg compounds such as the salts of the organic acids, the N — Hg compounds such as the mercury acid amide compounds, and the S — Hg compounds such as the mercuric mercaptides will be touched on very lightly as most of their properties are the properties of inorganic mercury salts. The great mass of biological and pharmacological studies which have been made on organic mercurials will not be included both because of lack of space and because of the unsatisfactory condition of the literature of this phase of the subject. Another subject of considerable interest which cannot be discussed is the host of "double compounds" of mercury compounds and organic substances. These subjects which are not discussed are made available for further study by the supplementary bibliographical lists in the Appendix. In this way the writer has attempted to include in one form or another all of the material which has been gathered in the preparation of the work.

The monograph will be arranged to serve both the general chemist who wishes to get a conception of what has been done in the field as a whole and the specialist who wishes to find out quickly what has been done in any particular portion of the field. In many cases unsettled points have been indicated. It is hoped that the work will inspire further research in this interesting field. It has been found necessary to omit practically all detailed experimental material. In general enough detail is given to make evident the method but not enough to serve as a laboratory guide in repeating any of the work. The lists of references given in the text contain the most important articles on the given subject. Many of the less important references have been omitted but will be found in the supplementary bibliographical lists.

The writer has a number of acknowledgments to make. Portions of the work have been done with aid from the libraries of the following institutions, University of Chicago, University of Minnesota, University of Wisconsin, Abbott Laboratories, and the John Crerar Library of Chicago. Valuable suggestions have been received from Professors Roger Adams, W. Lee Lewis, and A. S. Loevenhart. Dr. Austin M. Patterson has made many helpful suggestions for naming organic mercury compounds. Mr. Edmund B. Middleton, Research Assistant under the U. S. Interdepartmental Social Hygiene Board, has rendered invaluable assistance in arranging and checking the bibliographical material and in reading the proof.

F. C. W.

NORTHWESTERN UNIVERSITY,
Evanston, Illinois.

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TO

CHARLES LORING JACKSON

ORGANIC COMPOUNDS OF MERCURY

Chapter I.

Historical Outline of the Study of Organic Mercury Compounds.

In 1843 A. W. von Hofmann obtained a mercury compound from aniline and mercuric chloride.[1] To this day it is not certainly known whether this product had mercury attached to nitrogen or to carbon. If the latter is true this substance was the first compound containing the C — Hg linkage. In 1850 Frankland noted that ethyl iodide reacts with metallic mercury in sunlight giving gaseous products.[2] Two years later he found that methyl iodide reacts with mercury in sunlight forming the crystalline organomercuric compound, methyl mercuric iodide.[3]

$$CH_3-I+Hg\rightarrow CH_3-Hg-I$$ [4]

Soon other chemists turned their attention to mercury alkyl compounds. In 1854 Strecker made ethyl mercuric iodide by treating ethyl iodide with metallic mercury in diffused light.[5] He converted the iodide into other ethyl mercuric salts. In the same year Dünhaupt obtained ethyl mercuric chloride by heating bismuth triethyl with mercuric chloride.[6] Later Buckton made an extensive study of other methyl and ethyl mercuric compounds.[7]

In 1851 Sobrero and Selmi had introduced another type of organic mercury compound.[8] By heating mercuric chloride and potassium

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[1] *Ann.* 47 (1843), 62.

[2] *J. Chem. Soc.* 3 (1850), 322. *Ann.* 77 (1851), 225.

[3] *Ann.* 85 (1853), 361.

[4] Those less familiar with organic mercury compounds should note that the alkyl mercuric halides resemble the analogous Barbier-Grignard reagents in formula only. The physical and chemical properties of the two classes of compounds are entirely different.

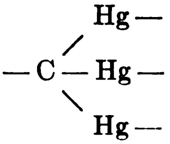
[5] *Ann.* 92 (1854), 75.

[6] *J. prakt. Chem.* (1) 61 (1854), 423. *Ann.* 92 (1854), 379.

[7] *Ann.* 108 (1858), 103; 109 (1859), 219; 112 (1859), 220.

[8] *Ann.* 80 (1851), 108.

hydroxide in alcohol they obtained a yellow slightly explosive substance containing mercury and carbon. Many of their contemporaries tried without success to make this explosive compound. Their work is of interest only as a forerunner of the extensive work of K. A. Hofmann on the mercarbides, compounds containing the grouping,



In 1855 Zinin found that allyl iodide unites with metallic mercury forming a crystalline compound even more rapidly than does methyl iodide.[9]

$$CH_2 = CH - CH_2 I + Hg \rightarrow CH_2 = CH - CH_2 - Hg - I.$$

The method of making alkyl mercury compounds by introducing mercury directly into alkyl iodides is very limited as only a few compounds give the reaction. A new and more general method of preparation was devised by Frankland and Duppa in 1863.[10] They found that methyl and ethyl iodides react with sodium amalgam in the presence of ethyl acetate forming mercury dimethyl and mercury diethyl.

$$2\ CH_3 - I + Hg + 2\ Na \rightarrow 2\ NaI + CH_3 - Hg - CH_3.$$

At this time Frankland studied the action of the mercury alkyls with various metals thus obtaining a number of other metal alkyls. In 1866 Chapman improved Frankland's method for making mercury alkyls by using bromides instead of iodides.[11] At this time Schorlemmer recommended the action of sulfuric acid with mercury diethyl for making pure ethane.[12]

$$2(C_2H_5)_2Hg + H_2SO_4 \rightarrow 2C_2H_6 + (C_2H_5 - Hg)_2SO_4.$$

In 1868 Otto treated bromonaphthalene with sodium amalgam to prepare dinaphthyl but instead obtained mercury dinaphthyl.[13] He extended Frankland's reaction to the aromatic series, and made a very careful study of the reactions of organic mercury compounds in general. Among the reactions which he studied are the following: the action of acids to form hydrocarbons and organomercuric salts; the

---

[9] *Ann.* 96 (1855), 363.

[10] *J. Chem. Soc.* 16 (1863), 415. *Ann.* 130 (1864), 104.

[11] *J. Chem. Soc.* 19 (1866), 150. *Ann.* 139 (1866), 128.

[12] *Ann.* 132 (1864), 234.

[13] *Ann.* 147 (1868), 164; 154 (1870), 188.

action of halogens to form organic halides and organomercuric halides or mercuric halides; with mercuric salts to form organomercuric salts; and with oxidizing agents to form organomercuric hydroxides. It is noteworthy that the compounds R — HgOH have strongly basic properties. These general reactions may be summarized by the following equations:

$$R-Hg-R + HX \rightarrow R-H + R-Hg-X$$
$$R-Hg-R + X_2 \rightarrow R-X + R-Hg-X$$
$$R-Hg-X + X_2 \rightarrow R-X + HgX_2$$
$$R-Hg-R + HgX_2 \rightarrow 2R-Hg-X$$ [14]
$$R-Hg-R + KMnO_4 \rightarrow R-Hg-OH$$

Dreher and Otto next studied mercury diphenyl and mercury ditolyl, prepared by the action of sodium amalgam and ethyl acetate on bromobenzene and p-bromotoluene.[15] They discovered, however, a limitation to Frankland's reaction when they tried to prepare mercury dibenzyl from benzyl bromide and sodium amalgam.

Mercury dibenzyl has since been prepared but only by means of the Grignard reagent.[16]

In 1869 Wurtz treated chloroformic ester and bromobenzene with sodium amalgam. Besides ethyl benzoate he obtained a by-product of mercury diphenyl.[17] In a similar way he obtained mercury ditolyl as a by-product of the action of sodium amalgam on a mixture of chloroformic ester and p-bromotoluene.

In 1871 Reynolds first studied the action of mercuric salts and alkali on acetone.[18] Although the complex mercury compounds obtained in this way have been studied by a number of investigators their structure is not yet established. In 1873 Cahours prepared and studied the mercury derivatives of propyl and isobutyl.[19] The next year Victor

---

[14] This is one of the most striking and general reactions of the organic mercury compounds, in which both bonds of the mercury are attached to carbon. Usually the reaction is brought about by the simple mixing of solutions of R_2Hg and the mercuric salt. In a few cases heat is required. In general the product of the reaction, R — Hg — X, is more insoluble than the compound R_2Hg or the mercuric salt. However, this insolubility does not seem to be the controlling cause of the change as the same reaction takes place in some instances in which R_2Hg is the more insoluble.

[15] *Ber.* 2 (1869), 542. *Ann.* 154 (1870), 93, 171. *J. prakt. Chem.* (2) 1 (1870), 179.

[16] Pope and Gibson, *J. Chem. Soc.* 101 (1912), 735. Wolff, *Ber.* 46 (1913), 64. Hilpert and Grüttner, *Ber.* 48 (1915), 906. L. W. Jones, *J. Am. Chem. Soc.* 40 (1918), 1257.

[17] *Compt. rend.* 68 (1869) 1298. *Ann. Spl.* 7 (1870), 124.

[18] *Ber.* 4 (1871), 483.

[19] *Compt. rend.* 76 (1873), 134; 77 (1873), 1405. *J. prakt. Chem.* (2) 8 (1873), 397.

Meyer made a mercury compound from nitromethane. Although this substance is not a true organic mercury compound, in that the mercury is attached to oxygen, it is mentioned because it played so important a part in the study of the structure of fulminic acid.[20] At this time Ladenberg found that mercury diphenyl reacts with silicon tetrachloride giving a phenyl silicon compound.[21]

$$SiCl_4 + C_6H_5 - Hg - C_6H_5 \rightarrow C_6H_5 - Hg - Cl + C_6H_5 - SiCl_3.$$

In 1876 Michaelis published the first results of his study of the aromatic compounds of the nitrogen group.[22] He first used mercury diphenyl and phosphorus trichloride.

$$PCl_3 + C_6H_5 - Hg - C_6H_5 \rightarrow C_6H_5 - Hg - Cl + C_6H_5 - PCl_2.$$

These studies were continued with results of the utmost importance to the study of organic arsenicals. In 1880 Oppenheim made the first mercury derivative of acetoacetic ester.[23] In 1880 Michaelis treated mercury diphenyl with arsenious chloride, obtaining two reactions, depending on the conditions.[24]

$$AsCl_3 + C_6H_5 - Hg - C_6H_5 \rightarrow C_6H_5 - Hg - Cl + C_6H_5 - AsCl_2.$$
$$2AsCl_3 + C_6H_5 - Hg - C_6H_5 \rightarrow HgCl_2 + 2C_6H_5 - AsCl_2.$$

In the same year Kutscheroff studied the effect of mercuric salts on allylene and acetylene.[25] The mercury compounds obtained are decomposed by acids giving the hydration products of the acetylene compounds, in these cases, acetone and acetaldehyde.

$$CH_3 - C \equiv CH \longrightarrow \text{Mercury compound.} \xrightarrow{\text{Acid}} CH_3 - CO - CH_3$$
$$CH \equiv CH \longrightarrow \text{Mercury compound.} \xrightarrow{\text{Acid}} CH_3 - CO - H.$$

In spite of the fact that some fifteen chemists have published work on the subject, the structure of the mercury compounds obtained from acetylene is not yet settled. However the reaction has acquired considerable commercial importance as it gives the means of converting acetylene into alcohol and acetic acid. At this time Michaelis contributed a new reaction to the chemistry of organic mercury by the

---

[20] Meyer, *Ann.* 171 (1874), 31. *Ber.* 5 (1872), 516. Nef, *Ann.* 280 (1894), 263. L. W. Jones, *Am. Chem. J.* 20 (1898), 33.

[21] *Ann.* 173 (1874), 151.

[22] *Ann.* 181 (1876), 288.

[23] *Ber.* 10 (1877), 701.

[24] *Ann.* 201 (1880), 184.

[25] *Ber.* 13 (1880), 17; 14 (1881), 1536; 17 (1884), 13.

discovery that aromatic boric acids react with mercuric chloride solution, giving aromatic mercuric chlorides.[26]

$$C_6H_5-B(OH)_2 + HgCl_2 + H_2O \rightarrow C_6H_5-Hg-Cl + H_3BO_3 + HCl.$$

A few years later Michaelis extended Frankland's reaction beyond the range of hydrocarbon derivatives, by treating p-bromodimethylaniline with sodium amalgam and ethyl acetate.[27] This reaction gave him a new type of mercury compound from which he made new aromatic derivatives of the nitrogen group of elements.

$$2(CH_3)_2N-C_6H_4-Br + Hg + 2Na \rightarrow$$
$$2NaBr + (CH_3)_2N-C_6H_4-Hg-C_6H_4-N(CH_3)_2$$

Michaelis next extended the reaction to phenol ethers using p-bromoanisole and sodium amalgam in the presence of ethyl acetate.[28]

In 1892 Pesci published the first of his many researches on the mercury derivatives of aniline and its substitution products.[29] Before this time he had been working on ammonia mercuric compounds. This, without doubt, led to his study of aniline mercury compounds and likewise to his misinterpretation of their structures and reactions.[30] In spite of these errors, Pesci's work has been of the greatest importance in the development of the chemistry of organic mercury. He was the first to realize that mercury could be introduced into the nucleus of an aromatic amine. Interpreted in modern formulas, Pesci's reaction between dimethylaniline and mercuric acetate becomes,

$$(CH_3)_2N-C_6H_5 + Hg(OAc)_2 \rightarrow (CH_3)_2N-C_6H_4-HgOAc + HOAc.$$

Although he misinterpreted the reaction, he made a careful study of the methods of changing compounds of the type $R-Hg-X$ to those of the type R_2Hg in which both bonds of mercury are attached to carbon. The reagents which he used most frequently were sodium sulfide and sodium thiosulfate. Again using the correct formulas, one of these reactions may be represented by the equation

$$2(CH_3)_2N-C_6H_4-HgOAc + 2Na_2S_2O_3 \rightarrow Na_2Hg(S_2O_3)_2 +$$
$$[(CH_3)_2N-C_6H_4-]_2Hg.$$

The compound obtained in this case proved to be identical with the product obtained by Michaelis from sodium amalgam and p-bromo-

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[26] *Ber.* 15 (1882), 180.

[27] *Ber.* 21 (1888), 1501; 23 (1890), 2342. *Ann.* 260 (1890), 6.

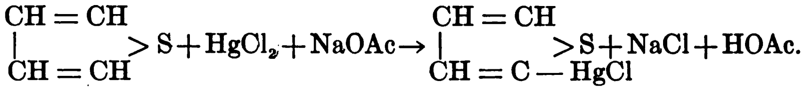
[28] *Ann.* 293 (1896), 196, 313.

[29] *Atti acad. Lincei* (5) II (1892), 312. *Gazz. chim. ital.* 22 I (1892), 373. *Chem. Zentr.* 1892 II 213. *Z. anorg. Chem.* 15 (1897), 208; 17 (1898), 276.

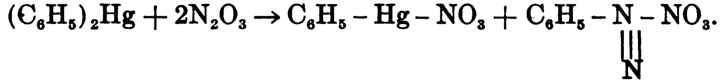
[30] Cf. *J. Am. Chem. Soc.* 41 (1919), 1842.

dimethylaniline. This identity proves that the mercuration of the aromatic amine with mercuric acetate takes place in the para position to the dimethyl-amino group.

In the same year that Pesci made his discovery, Volhard independently discovered the direct replacement of hydrogen by mercury. He found that thiophene reacts with mercuric salts, giving a product having mercury in the alpha position.[31]

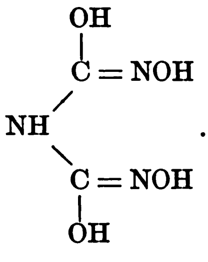


In 1894 Desesquelle prepared mercury derivatives of phenols and naphthols.[32] He misinterpreted the structure of many of these substances by assuming that the mercury must be attached to oxygen. In all probability it is attached to carbon and they are therefore true organic mercury compounds. In 1897 Bamberger discovered a new reaction of organic mercury compounds when he treated mercury diphenyl with nitrous anhydride obtaining benzene diazonium nitrate.[33]



$$(C_6H_5)_2Hg + 2N_2O_3 \rightarrow C_6H_5-Hg-NO_3 + C_6H_5-\underset{\underset{N}{|||}}{N}-NO_3.$$

He applied this reaction to mercury dimethyl, hoping to obtain an aliphatic diazonium compound, but instead, he obtained imidodihydroximic acid,



In 1898 Dimroth first showed that mercuration [34] of aromatic compounds is as general a process as nitration or sulfonation. Pesci's work

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[31] *Ann.* 267 (1892), 172.

[32] *Bull. soc. chim.* (3) 11 (1894), 263.

[33] *Ber.* 30 (1897), 509; 31 (1898), 1528; 32 (1899), 3546. Cf. *Chem. Zentr.* 1898 II 1015.

[34] Some chemists prefer the longer term "mercurization." Apparently the only authority for this is found in Patterson's "German-English Dictionary for Chemists" in which "merkurieren" is translated "mercurize." Undoubtedly this is a more literal translation of the German word than "mercurate." Dr. Patterson in a private com-

had been confined to the aromatic amines and his interpretation of the reactions had been faulty. Dimroth showed that mercuric acetate introduces the acetoxymercuri group, — HgOAc, into a great variety of aromatic compounds including hydrocarbons, phenols, and nitrobenzene.[35] He interpreted all of the reactions correctly, and showed the errors in Pesci's work. Some of Dimroth's results may be illustrated by the equations—

$$C_6H_6 + Hg(OAc)_2 \xrightarrow{110^\circ} C_6H_5 - HgOAc + HOAc.$$

$$CH_3 - C_6H_5 + Hg(OAc)_2 \xrightarrow{\text{Reflux}} CH_3 - C_6H_4 - HgOAc + HOAc.$$

Mixture of o- and p-

$$C_6H_5 - NH_2 + Hg(OAc)_2 \xrightarrow[\text{Alcohol}]{\text{Cold}} AcOHg - C_6H_4 - NH_2 + HOAc.$$

o- and p-

$$C_6H_5 - OH + Hg(OAc)_2 \xrightarrow[\text{Water}]{\text{Cold}} AcOHg - C_6H_4 - OH$$

Mixture of o- and p-

$$+ (AcOHg)_2C_6H_3 - OH + HOAc.$$

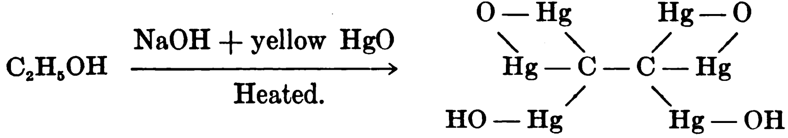
o, p-Compound.

$$C_6H_5 - NO_2 + Hg(OAc)_2 \xrightarrow{\text{Reflux}} AcOHg - C_6H_4 - NO_2 + HOAc.$$

ortho compound.

It will be noticed that the mercuration reactions follow the ordinary rules for orientation except in the case of nitrobenzene. It is a general fact that groups like the nitro and carboxyl groups, which usually direct the entering group to the meta position, are mercurated in the ortho position instead.

In the same year that Dimroth published his first results, K. A. Hofmann started his study of the mercarbides, compounds in which all of the hydrogens of a methyl group are replaced by mercury.[36] Ethyl alcohol yields ethane hexamercarbide.



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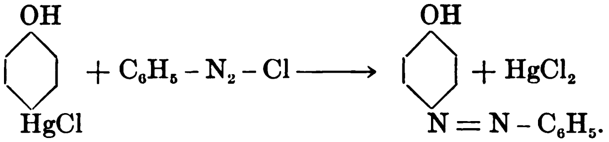
munication expresses a slight preference for the form of the verb, "to mercurate." This form is used because it suggests the similarity of the process to those reactions which are indicated by the verbs "to brominate," "to nitrate," etc. Moreover "mercurize" suggests the pharmacist's processes involving the physical incorporation of materials with metallic mercury.

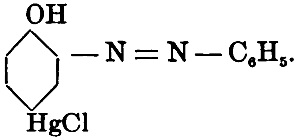
[35] *Ber.* 31 (1898), 2154; 32 (1899), 758. Habilitationsschr. Tübingen (1900), *Chem. Zentr.* 1901 I 449-454. *Ber.* 35 (1902), 2044, 2853.

[36] *Ber.* 31 (1898), 2624; 33 (1900), 1328; 38 (1905), 3654.

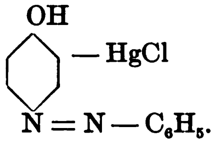
Bamberger prepared mercury derivatives of beta-naphthol by means of mercuric acetate. He also discovered that diazonium salts react with mercurated phenols replacing the mercury by the benzeneazo group if the mercury occupies the position normally involved in the coupling reactions of the free phenol.[37] This reaction may be illustrated by the equations involving mercurated phenols later studied by Dimroth.



Part of the coupling takes place in the ortho position giving a small amount of an azo compound still containing mercury,



If the position in which the coupling takes place is unsubstituted the coupling is completed without the removal of the mercury from the nucleus. Thus an ortho-mercurated phenol would give a compound,



In 1899 Denigès published a classification of mercury compounds and the results of a study of the action of mercuric salts on ethylene compounds.[38]

In 1900 Hofmann and Sand published the first of a lengthy series of papers on the action of mercuric salts with ethylene and other unsaturated compounds.[39] Biilmann disagreed with some of the results obtained by these investigators.[40] In general the reaction of a mercuric salt with an ethylene compound in the presence of water, con-

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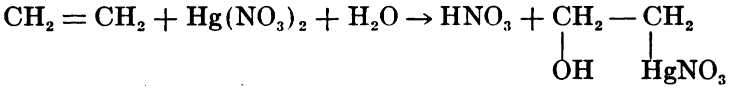
[37] *Ber.* 31 (1898), 2624.

[38] *Ann. chim. phys.* (7) 18 (1899), 382-432. *Bull. soc. chim.* (3) 19 (1898), 494.

[39] *Ber.* 33 (1900), 1340, 1358, 2692; 34 (1901), 1385, 2906.

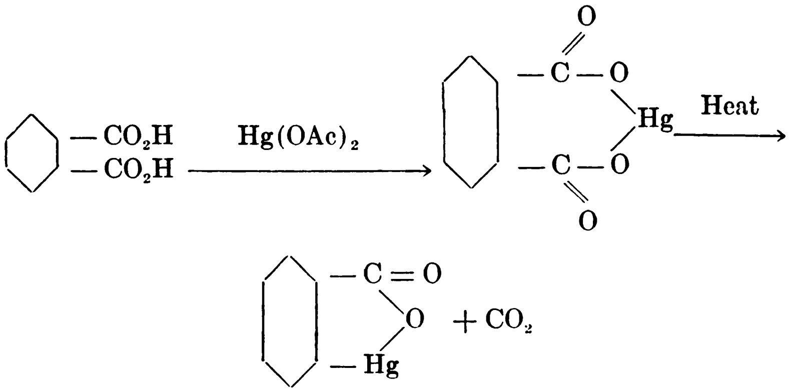
[40] *Ber.* 33 (1900), 1641; 35 (1902), 2586.

sists in the addition of the groups —OH and —HgX to the double bond. Various more complicated compounds are also obtained. The simplest reaction is as follows:



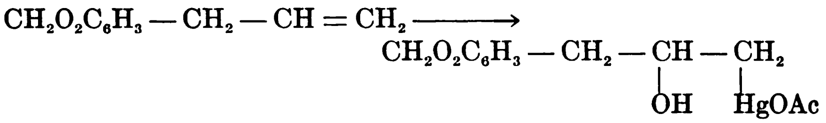
$$CH_2 = CH_2 + Hg(NO_3)_2 + H_2O \rightarrow HNO_3 + \underset{OH}{\underset{|}{CH_2}} - \underset{HgNO_3}{\underset{|}{CH_2}}$$

In 1901 Pesci[40a] replaced a carboxyl group by mercury by heating phthalic acid with mercuric acetate. The reaction probably takes place as follows:



Pesci did not realize that this reaction could be extended to the preparation of other mercury compounds. Recently Kharasch has extended this reaction to a great variety of compounds making available types of mercury compounds which can be obtained in no other way.[40b]

In 1902 Balbiano and Paolini, while using mercuric acetate solution as an oxidizing agent, discovered that it gives mercury derivatives with the allyl compounds of phenol ethers. The reaction with a substance like safrol consists in the addition of the groups —OH and —HgOAc to the double bond.[41]



$$CH_2O_2C_6H_3 - CH_2 - CH = CH_2 \longrightarrow CH_2O_2C_6H_3 - CH_2 - \underset{OH}{\underset{|}{CH}} - \underset{HgOAc}{\underset{|}{CH_2}}$$

The corresponding propenyl compounds such as isosafrol give no mercury compounds but undergo oxidation with the formation of glycols.

[40a] *RAL.* (5) 10 I (1901), 362.

[40b] Private communication, M. S. Kharasch, University of Chicago.

[41] *Ber.* 35 (1902), 2994; 36 (1903), 3575.

The group $—CH = CH — CH_3$ changes to $—CHOH — CHOH — CH_3$ and mercurous acetate precipitates.

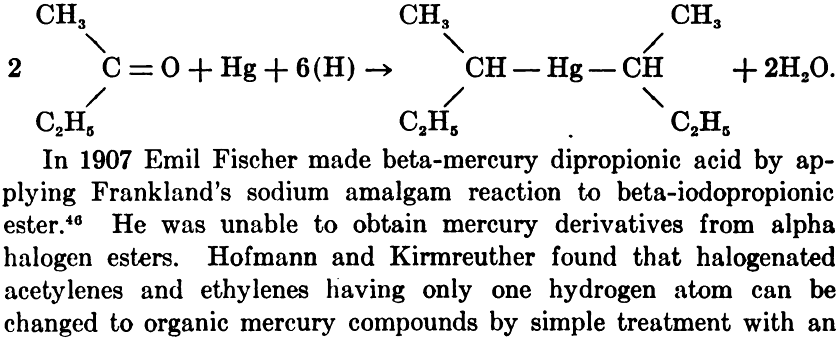
In 1904 Pfeiffer and Truskier applied the Grignard reagent to the preparation of organic mercury compounds.[42] They prepared mercury diphenyl from phenyl magnesium bromide and mercuric chloride according to the equation,

$$2C_6H_5 - Mg - Br + HgCl_2 \rightarrow C_6H_5 - Hg - C_6H_5 + HgBr_2 + MgCl_2.$$

The next year Peters discovered a new preparation of aromatic mercury compounds by heating a sulfinic acid with mercuric chloride.[43]

$$C_6H_5 - SO_2H + HgCl_2 \rightarrow C_6H_5 - Hg - Cl + SO_2 + HCl.$$

In 1908 Hantzsch and Auld published a study of the mercury derivatives of nitro phenols.[44] This work gave some interesting results bearing upon the relation between quinoid structure and color. Tafel discovered a new method for making certain mercury dialkyls during some experiments on the reduction of ketones in acid solution with a mercury cathode. The reduction of acetone and methyl ethyl ketone gives mercury di-isopropyl and mercury di-secondary-butyl.[45] The formation of the latter substance may be represented as follows:



$$2\ \overset{CH_3}{\underset{C_2H_5}{>}}C = O + Hg + 6(H) \rightarrow \overset{CH_3}{\underset{C_2H_5}{>}}CH - Hg - CH\overset{CH_3}{\underset{C_2H_5}{<}} + 2H_2O.$$

In 1907 Emil Fischer made beta-mercury dipropionic acid by applying Frankland's sodium amalgam reaction to beta-iodopropionic ester.[46] He was unable to obtain mercury derivatives from alpha halogen esters. Hofmann and Kirmreuther found that halogenated acetylenes and ethylenes having only one hydrogen atom can be changed to organic mercury compounds by simple treatment with an alkaline solution of mercuric cyanide.[47] Trichloroethylene acts as follows:

$$2Cl_2C = CHCl + Hg(CN)_2 + 2KOH \rightarrow 2KCN + (Cl_2C = CCl)_2Hg.$$

In 1908 Schoeller and Schrauth published the first of their long series of papers covering almost all types of organic mercury com-

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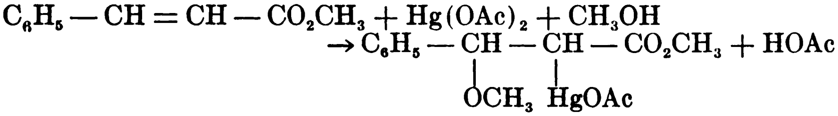
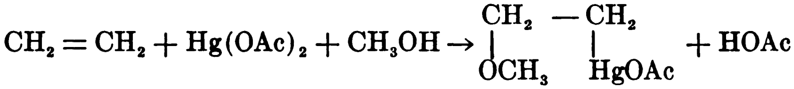
[42] *Ber.* 37 (1904), 1125.
[43] *Ber.* 38 (1905), 2567.
[44] *Ber.* 39 (1906), 1105.
[45] *Ber.* 39 (1906), 3626.
[46] *Ber.* 40 (1907), 386.
[47] *Ber.* 41 (1908), 314; 42 (1909), 4232.

pounds. Their first study was on mercury malonic ester and its hydrolysis.[48] Biilmann discovered that allocinnamic acid gives an organic mercury compound with mercuric acetate, whereas common cinnamic acid does not.[49] The product is an inner salt or anhydride of α-hydroxymercuri-β-hydroxy-hydrocinnamic acid. As in the case of the ethylene hydrocarbons the reaction consists in the addition of the hydroxyl and hydroxymercuri groups to the double bond. In 1910 Schoeller and Schrauth applied Biilmann's discovery of the action of mercuric acetate with allocinnamic acid to methyl cinnamate. In methyl alcohol solution a compound is formed which has a methoxy group and an acetoxymercuri group added to the double bond.[50]



$$\mathrm{C_6H_5-CH=CH-CO_2CH_3+Hg(OAc)_2+CH_3OH} \rightarrow \mathrm{C_6H_5-}\underset{\mathrm{OCH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{-}\underset{\mathrm{HgOAc}}{\underset{|}{\mathrm{CH}}}\mathrm{-CO_2CH_3+HOAc}$$

In the next few years they extended their studies to the mercury compounds of alpha-anilino acids,[51] toluidines and toluidides,[52] anthranilic esters,[53] and pyrazolones.[54] They also found that ethylene reacts with an alcoholic solution of mercuric acetate much as does methyl cinnamate.[55]



$$\mathrm{CH_2=CH_2+Hg(OAc)_2+CH_3OH} \rightarrow \begin{array}{cc} \mathrm{CH_2} & \mathrm{-CH_2} \\ | & | \\ \mathrm{OCH_3} & \mathrm{HgOAc} \end{array} \mathrm{+HOAc}$$

In 1913 Kraus electrolyzed solutions of alkyl mercuric halides in liquid ammonia. He obtained a number of the free radicals or complex metals, R — Hg —.[56] He found them to be unstable, readily changing to free mercury and a mercury dialkyl when allowed to warm up to room temperature. In the same year von Braun studied the action of sodium amalgam on dibromides and obtained compounds containing mercury as a member of a heterocyclic ring.[57] An example of these substances is the compound obtained from pentamethylene di-

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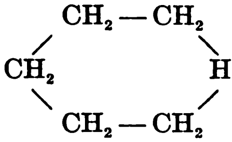
[48] *Ber.* 41 (1908), 2087.
[49] *Ber.* 41 (1908), 4340. *Ber.* 43 (1910), 568.
[50] *Ber.* 43 (1910), 695; 44 (1911), 1048, 1432.
[51] *Ber.* 44 (1911), 1300.
[52] *Ber.* 45 (1912), 2808.
[53] *Ber.* 47 (1914), 1930.
[54] *Ber.* 47 (1914), 2736.
[55] *Ber.* 46 (1913), 2864.
[56] *J. Am. Chem. Soc.* 35 (1913), 1732.
[57] *Ber.* 46 (1913), 1792; 47 (1914), 490.

bromide,  These substances are hard to obtain in monomolecular form as they polymerize readily. Hilpert and Ditmar found that aluminum carbide can be used with mercuric chloride to form methyl mercuric chloride or mercury dimethyl.[58] Hilpert and Grüttner studied "mixed" mercury alkyls and aryls in which the two bonds of the mercury are attached to different hydrocarbon residues. These substances are extraordinarily unstable, readily changing to a mixture of the two simple compounds, R_2Hg and R'_2Hg.[59] In this same year Brieger and Schulemann published an extended study of the mercuration of the naphthalene intermediates of the coal-tar dye industry. In many cases they were unable to obtain mercurated products as the intermediates were oxidized by the mercuric salts.[60] In 1916 Grignard and Abelmann applied the Grignard reaction to mercurated ketones, obtaining mercurated tertiary alcohols.[61] In 1918 L. W. Jones published a paper on the electronic nature of the $C - Hg$ bonds in the mercury dialkyls and similar compounds.[62] He advanced evidence to show that the two benzyl groups in mercury dibenzyl are of opposite charge, as they are removed by hydrolysis in the form of toluene and benzyl alcohol respectively. This would indicate that the mercury atom is $\overset{+\,-}{Hg}$, at least at the instant splitting takes place.[63] This is in harmony with the fact that the mercury appears as the free metal at the end of the reaction. In 1920 Kharasch and Piccard published preliminary results on the preparation of some dyes containing mercury.[64] Manchot has recently published a series of papers to prove that the many organic mercury compounds obtained from unsaturated compounds are mere molecular compounds having no structural relation between the unsaturated carbon atoms and the groups — HgX and — OH or — OR which appear in the products.[65] The simplest compound of ethylene with a mercuric salt would thus be

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[58] *Ber.* 46 (1913), 3738.

[59] *Ber.* 47 (1914), 177, 186.

[60] *J. prakt. Chem.* (2) 89 (1914), 97.

[61] *Bull. soc. chim.* (4) 19 (1916), 18.

[62] *J. Am. Chem. Soc.* 40 (1918), 1257.

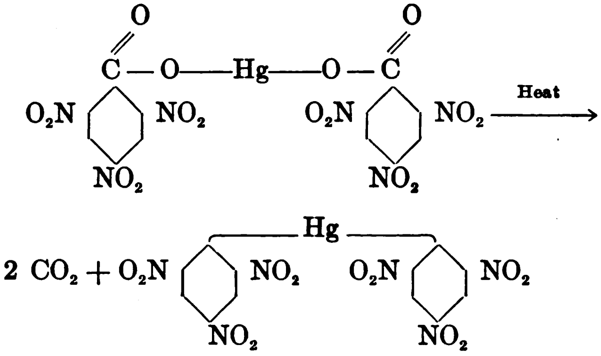
[63] Compare Kharasch, *J. Am. Chem. Soc.* 43 (1921), May ?.

[64] *J. Am. Chem. Soc.* 42 (1920), 1861.

[65] *Ber.* 53 (1920), 984. *Ann.* 421 (1920), 316, 331.

$C_2H_4.Hg(OH)X$. Much more experimental work must be forthcoming before the problem of the true nature of these compounds is settled.

Recently Kharasch[66] has shown that acids which lose carbon dioxide readily on heating form mercuric salts which also lose carbon dioxide on heating. Compounds of the type R_2Hg are usually obtained. The reaction has been applied to a great variety of mercuric salts. It may be illustrated by the following case:



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[66] Private communication.

Chapter II.

General Methods of Preparing Organic Mercury Compounds.

I. Preparation from Organic Halides.

Among the many general methods for the introduction of mercury into organic compounds are the three following, each of which starts with an organic halide; the action of free mercury on an alkyl iodide, the action of sodium amalgam on an organic iodide or bromide, and the action of a mercuric halide on a Grignard reagent.

A. *Reaction of Metallic Mercury with Alkyl Iodides.*

In this reaction the iodide adds to the mercury giving a substance which has one bond of the mercury attached to carbon and the other attached to iodine. Thus methyl iodide reacts readily with metallic mercury in sunlight giving a crystalline mass of methyl mercuric iodide.

$$CH_3 - I + Hg \rightarrow CH_3 - Hg - I.$$

When ethyl iodide is used the reaction must be carried out in diffused light as direct sunlight decomposes ethyl mercuric iodide. The higher alkyl iodides probably react much more slowly with mercury but no accurate study of the subject has been made. The bromides and chlorides do not react with metallic mercury in this way. The unsaturated iodides, allyl iodide and propargyl iodide, unite with mercury even more readily than methyl iodide forming the compounds $CH_2 = CH - CH_2 - HgI$ and $CH \equiv C - CH_2 - HgI$. Methylene iodide rapidly forms iodomethyl mercuric iodide, $I - CH_2 - HgI$, or methylene mercuric iodide, $CH_2(HgI)_2$, depending on the amount of mercury used.

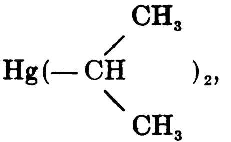
B. *Reaction of Sodium Amalgam with Organic Iodides and Bromides.*

The product of this reaction differs from that obtained from metallic mercury in having both bonds of the mercury attached to carbon. The reaction takes place only in the presence of an ester like methyl or ethyl acetate. At the end of the reaction the ester can be recovered unchanged. There is no satisfactory explanation for this catalytic action of the ester. Methyl iodide reacts rapidly with cold very dilute sodium amalgam forming mercury dimethyl.

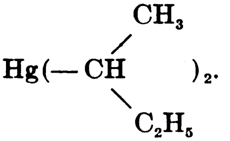
$$2CH_3-I + 2Na + Hg \rightarrow CH_3-Hg-CH_3 + 2NaI.$$

This reaction takes place very readily in the aliphatic series. The best yields are obtained at a low temperature with amalgams containing only about 0.1 per cent of sodium. In the aromatic series more concentrated amalgams and higher temperatures must be used.

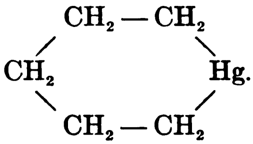
In the aliphatic series the reaction has been used with bromides or iodides of methyl, ethyl, n-propyl, isobutyl, isoamyl, and octyl. Secondary iodides react vigorously with sodium amalgam but form no organic mercury compounds. The mercury secondary alkyls which would be expected have only been obtained as by-products in the reduction of ketones in acid solution with a mercury cathode. In this way acetone and methyl ethyl ketone give small amounts of mercury di-isopropyl,



$Hg(-CH(CH_3)_2)_2$, and mercury di-*secondary*-butyl,



$Hg(-CH(CH_3)(C_2H_5))_2$. The failure to obtain these substances by the sodium amalgam method may be due to their easy change to the corresponding hydrocarbons. There is one case, however, in which a secondary iodide gives an organic mercury compound. Cyclohexyl iodide reacts with sodium amalgam forming cyclohexyl mercuric iodide instead of the expected mercury di-cyclohexyl. Apparently the sodium does not take part in the reaction.

The reaction of several aliphatic dihalides with sodium amalgam has been studied. Ethylene dibromide and trimethylene dibromide react but give no organic mercury compounds. Tetramethylene di-iodide and pentamethylene dibromide or di-iodide react more vigorously with dilute sodium amalgam than does methyl iodide. The products are compounds containing mercury as a member of a heterocyclic ring. Pentamethylene dibromide gives three isomeric products having the composition $C_5H_{10}Hg$ and molecular weights corresponding to one, four, and six of these simple molecules. The simplest substance is a six membered ring containing mercury,  The tendency of this substance to polymerize resembles that of the cyclic ethers and sulfides.

In the aromatic series the sodium amalgam reaction has been used with monobromobenzene and the bromides of a great variety of benzene homologs. These include almost all of the possible methyl, dimethyl, and trimethyl benzenes as well as n-propyl benzene, p-cymene, and pentamethyl benzene. The products are mercury diphenyl and its homologs. Mono- and dibromodiphenyls give very insoluble mercury compounds which have not been carefully studied. The α and β-naphthyl bromides and iodides give the corresponding mercury dinaphthyls when heated with 4 per cent sodium amalgam.

The reaction has been extended to include halides other than those of the hydrocarbons. In the aliphatic series β-iodopropionic ester gives β-mercury bis-propionic ester, $Hg(CH_2 - CH_2 - CO_2Et)_2$. Alpha halogen esters give no mercury compounds by this reaction. In the aromatic series mercury compounds have been obtained from bromides of dimethyl aniline, diethyl aniline, dimethyl-p-toluidine, the anisoles, and the phenetoles.

Many cases have been observed in which the action of halides and sodium amalgam fails to give the desired products. Hydrogen iodide reacts vigorously with sodium amalgam in the presence of ethyl acetate but gives no mercury hydride. In general an unusually active halide does not give a mercury compound with sodium amalgam. Examples of such compounds are alpha halogen esters, benzyl halides, and phenacyl halides, $C_6H_5 - CO - CH_2X$. The action of a halogen atom attached to an unsaturated carbon has been studied in only one case. The compound $C_6H_5 - CH = C(Br) - CH(OAc) - CH_3$ reacts with the amalgam but gives no definite product.[1] As would be expected, the sodium amalgam reaction fails when applied to bromides containing groups which react with sodium such as the amino, hydroxyl, nitro, and carboxyl groups. The reaction also fails with chlorides.

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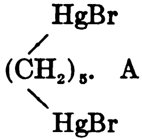
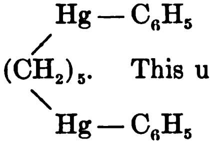
[1] Sand and Singer, *Ber.* 35 (1902), 3170.

C. *Reaction of Mercuric Halides with the Grignard Reagent.*

This action takes place on heating and gives a product which has one or both bonds of the mercury attached to carbon depending on the proportions of the reagents used.

$$CH_3 - Mg - I + HgI_2 \rightarrow CH_3 - Hg - I + HgI_2$$
$$2CH_3 - Mg - I + HgI_2 \rightarrow CH_3 - Hg - CH_3 + 2MgI_2.$$

In general a much better yield is obtained in the first reaction. This method has been little used in the aliphatic series as the mercury alkyls have not been studied much since the introduction of the Grignard reagent. Mercury dimethyl is most conveniently prepared by this method using mercuric chloride and an excess of methyl magnesium iodide.[2]

The Grignard reagent obtained from pentamethylene dibromide reacts with mercuric bromide giving pentamethylene di-mercuric bromide,  $(CH_2)_5\!\left\langle\begin{array}{l}HgBr\\HgBr\end{array}\right.$. A further use of the Grignard reagent may be made by heating this compound with phenyl magnesium bromide which gives the complex compound,  $(CH_2)_5\!\left\langle\begin{array}{l}Hg - C_6H_5\\Hg - C_6H_5\end{array}\right.$. This use of a second Grignard reagent, $R' - Mg - X$, on an organic mercuric halide, $R - Hg - X$, does not always produce the desired "mixed" organic mercury compound $R - Hg - R'$. In most cases the resulting product is a mixture of the two simple mercury compounds R_2Hg and R'_2Hg. This is the case in the action of o-tolyl mercuric bromide and p-tolyl magnesium bromide. The "mixed" compound expected is probably formed but at once changes to a mixture of the simple substances.

In addition to these preparations the Grignard reagent has been used to make mercury compounds of phenyl, p-tolyl, α-naphthyl, cyclohexyl, and benzyl. It gives the only means of making mercury compounds of the last mentioned group.

The fact that the Grignard reagent does not react with the grouping $C - Hg - X$ until heated makes it possible to convert mercurated

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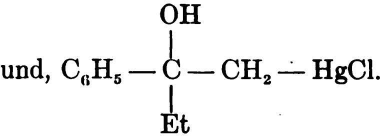
[2] Private communicaton from C. S. Marvel, University of Illinois.

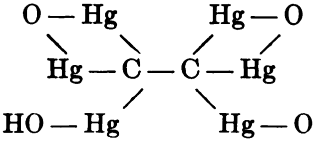
ketones to the corresponding mercurated tertiary alcohols. Thus phenacyl mercuric chloride reacts with ethyl magnesium bromide giving the compound,



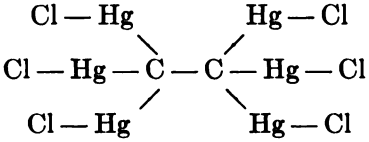
$$C_6H_5-\underset{Et}{\overset{OH}{C}}-CH_2-HgCl.$$

II. Mercuration by Means of Mercuric Oxide.

An entirely different method of introducing mercury into organic compounds involves the action of mercuric oxide, alone or with a base, on certain oxygen compounds such as alcohols, ketones, aldehydes, malonic esters, and acetoacetic ester. In the case of ethyl alcohol treatment with mercuric oxide and sodium hydroxide gives ethane hexamercarbide, $C_2Hg_6O_4H_2$, a mercarbide being a substance having all the hydrogen of a methyl group replaced by mercury. The mercarbide just mentioned may be regarded as a dehydration product of a substance having six — HgOH groups attached to two carbon atoms. This conception is strengthened by the fact that treatment with hydrochloric acid gives a substance $C_2Hg_6Cl_6$. The structures of the two substances are thus



and



The former compound on heating to about 230° changes color and then explodes with a brisant effect greater than that of mercury fulminate. The hexachloride is not explosive. Other mercarbides and less highly mercurated compounds have been obtained by the action of mercuric oxide and a base on aldehydes and ketones. In most cases the constitutions of these substances have not been definitely established.

Acetoacetic ester and malonic esters react with mercuric oxide giving compounds having mercury substituted for hydrogen of the methylene group. Malonic ester gives mercury bis-malonic ester. When this is hydrolyzed and heated it does not give the expected mercury bisacetic acid but gives an internal salt of hydroxymercuri[3] acetic acid, $HO-Hg-CH_2-CO_2H$. The use of methyl malonic ester in a

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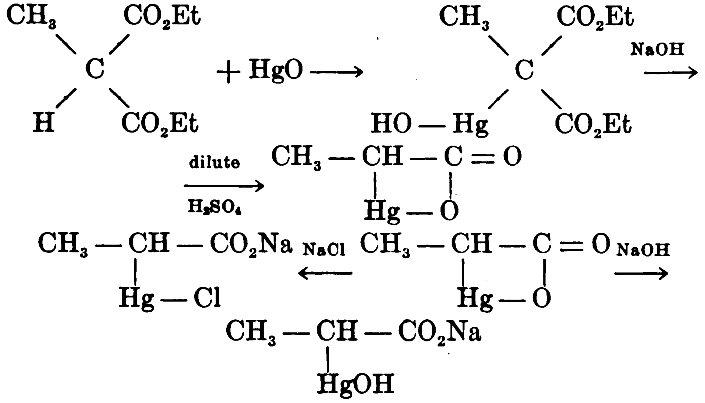
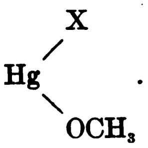
[3] In some cases the ordinary method of naming organic mercury salts as modified mercuric salts leads to awkward names. In the above case the ordinary system of

similar series of reactions gives a derivative of α-mercurated propionic acid. Thus these reactions make available the alpha mercurated compounds which cannot be made from the alpha-brom esters by the ordinary methods. The reactions involved in making the salts of α-hydroxymercuri propionic acid would be



III. Mercuration of Unsaturated Compounds.

Still a third general method for preparing organic mercury compounds is by treating unsaturated compounds with mercuric salts in aqueous or alcoholic solution. The reaction of an olefine compound with an aqueous mercuric salt consists in the addition of the groups —HgX and —OH to the double bond. In methyl alcohol solution the groups added are —HgX and —OCH_3. Some authorities claim that these addition products are not true "structural" compounds but molecular compounds of one molecule of the ethylene compound and one molecule of a basic mercuric salt or of a hypothetical substance  . Neither of these theories explains all of the reactions of the addition compounds.

naming would give "acetic acid mercuric hydroxide," "carboxymethyl mercuric hydroxide," or some other name which is either cumbersome or fails to emphasize the true nature of the compound. In such cases it seems best to give a name to the mercury group. Thus —HgOH is the "hydroxymercuri" group, —Hg—OAc is the "acetoxymercuri" group, —HgCl "chloromercuri," etc. In a few cases this system fails to give entirely euphonious names. Thus —Hg—ClO_3 must be called the "chloratemercuri" group.

Ethylene reacts with aqueous mercuric salts under suitable conditions giving a mercurated ethyl alcohol or a di-mercurated diethyl ether. The reactions may be summarized as follows:

$$CH_2 = CH_2 + HgX_2 + H_2O \rightarrow XHg - CH_2 - CH_2 - OH + HX.$$
$$2CH_2 = CH_2 + 2HgX_2 + H_2O \rightarrow$$
$$XHg - CH_2 - CH_2 - O - CH_2 - CH_2 - HgX + 2HX.$$

The mercurated products have been changed to ethyl alcohol, ethylene iodhydrine, and ββ′-di-iododiethyl ether. This would settle the constitution of the substances except for the fact that both of them react with hydrochloric acid or alkyl halides giving quantitative yields of ethylene. The only way to reconcile this formation of ethylene with the structures used is to assume that the mercury in the grouping Hg — C — C — O has some "loosening" or "activating" effect on the oxygen. Of course the production of ethylene is easily explained by the "molecular addition" formulas, $C_2H_4.Hg(OH)X$ and $2C_2H_4.HgO.HgX_2$. These, however, fail to explain the other reactions of the substances.

Methyl alcohol solutions of mercuric salts absorb ethylene very much more rapidly then the aqueous solutions.

$$CH_2 = CH_2 + HgX_2 + CH_3OH \rightarrow XHg - CH_2 - CH_2 - OCH_3 + HX.$$

The homologs of ethyl alcohol give similar reactions. The mercurated products give ethylene with acids and alkyl halides, thus making possible the formulation $C_2H_4.Hg(OCH_3)X$.

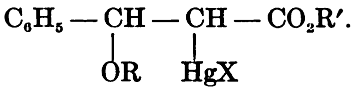
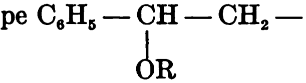
The reaction of aqueous mercuric salts has been studied with propylene, butylene, and a number of their higher homologs. Similar reactions take place with allyl alcohol and the common unsaturated acids. An exception is found in the case of the trans isomers such as fumaric acid and common cinnamic acid. These substances give no addition products with mercuric salts while their cis isomers, maleic acid and allocinnamic acid, readily add the groups — HgX and — OH.

Another failure of this reaction is noted in the case of propenyl phenyl derivatives such as isosafrol. Here the mercuric salt acts as an oxidizing agent forming a glycol.

$$CH_2O_2 = C_6H_3 - CH = CH - CH_3 \longrightarrow$$
$$CH_2O_2 = C_6H_3 - CHOH - CHOH - CH_3$$

This is in sharp contrast to the action of the corresponding allyl compounds such as safrol which add the groups — HgX and — OH in the usual way except that two isomeric products are obtained. Their occurrence may be due to the addition of the groups in the two possible ways although all other cases which have been studied indicate that this addition follows Markownikoff's rule, the mercury going to the carbon having the most hydrogen atoms.

The addition of mercuric salts to double bonds takes place in complicated compounds in much the same way as it does with ethylene. Thus terpineol and the similar open chain compound, dimethyl heptenol, give two sets of compounds, one containing an —OH group in addition to the one originally present, and the other containing an ether linkage formed by the elimination of water between the two hydroxyl groups.

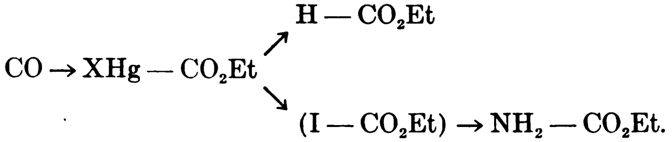
Various esters of cinnamic acid have been treated with mercuric acetate in solution in methyl, ethyl, n-propyl, and isopropyl alcohols. The products have the general formula  $C_6H_5-\underset{OR}{\underset{|}{CH}}-\underset{HgX}{\underset{|}{CH}}-CO_2R'$. When treated with ammonia and hydrogen sulfide in alcohol solution they give mercuric sulfide and alkoxyl hydrocinnamic esters of the type  $C_6H_5-\underset{OR}{\underset{|}{CH}}-CH_2-CO_2R'$, a reaction which makes it difficult to explain the mercurated esters as mere "molecular compounds."

Acetylene, its homologs, and phenyl acetylene react readily with mercuric salts. The nature of the products is still unsettled although there is some evidence that they contain a mercarbide grouping, i.e., a completely mercurated methyl group. Other investigators believe that these products are molecular compounds of mercury acetylides and basic mercuric salts. The following explanation of the action of mercuric chloride with acetylene is as plausible as any.

$$CH\equiv CH \rightarrow ClHg-CH=CH-Cl \rightarrow (ClHg)_2CH-CHCl_2 \rightarrow$$
$$(ClHg)_2CH-CHO \rightarrow (ClHg)_3C-CHO.$$

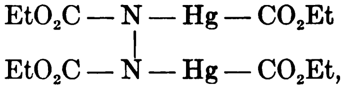
Whatever the doubt about the structure of the mercury compounds it is definitely established that treatment with acid gives a hydration product of the original acetylene. This change from acetylene to acetaldehyde is becoming commercially important as a step in the preparation of alcohol and acetic acid from inorganic materials.

Carbon monoxide behaves like an unsaturated compound with mercuric salts. When treated with mercuric acetate in alcohol it gives mercurated formic esters by the addition of the $-HgOAc$ and $-OR$ groups. Reduction by amalgamated aluminum gives a pure formic ester. Treatment with iodine and then with ammonia gives urethane.



$$\begin{tikzcd}[column sep=small] & & H-CO_2Et \\ CO \arrow[r] & XHg-CO_2Et \arrow[ur] \arrow[dr] & \\ & & (I-CO_2Et) \arrow[r] & NH_2-CO_2Et. \end{tikzcd}$$

Such reactions are hard to explain on the basis of molecular addition formulas. On the other hand it is hard to see from the structure formulas why the mercurated formic ester should react with halogen acids and alkyl halides, giving carbon monoxide quantitatively. Recent work makes it appear that this formation of carbon monoxide is a property of the grouping $-Hg-CO_2R$. The compound,



$$\begin{array}{l} EtO_2C-N-Hg-CO_2Et \\ | \\ EtO_2C-N-Hg-CO_2Et, \end{array}$$

reacts with hydrochloric acid giving exactly two molecules of carbon monoxide.[4]

IV. Mercuration of Halogenated Acetylenes and Ethylenes.

A few unsaturated compounds can be mercurated without involving the multiple bond. Such compounds are the halogenated ethylenes and acetylenes which have only one remaining hydrogen. These substances react with an alkaline solution of mercuric cyanide, giving compounds in which both bonds of the mercury are attached to carbon. Thus monochloroacetylene gives mercury bis-monochloroacetylene, $Hg(C\equiv C-Cl)_2$, and trichloroethylene gives a corresponding compound, $Hg(-\overset{\overset{\displaystyle Cl}{|}}{C}=CCl_2)_2$. The bromine compounds have also been made. None of these compounds has been carefully studied.

V. Mercuration of Aromatic Compounds.

The most fruitful method of introducing mercury into organic compounds has been the direct mercuration of aromatic compounds by mercuric acetate. This substance reacts readily with a great variety of compounds, $R-H$, in which R represents a substituted or un-

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[4] Diels and Uthemann, *Ber.* 53 (1920), 725.

substituted aromatic residue. The process bears a certain resemblance to hydrolysis as may be shown by the equations

$$R - H + Hg(OAc)_2 \rightarrow R - HgOAc + HOAc.$$
$$HO - H + Hg(OAc)_2 \rightarrow HO - HgOAc + HOAc.$$

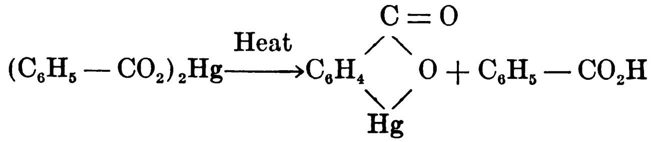
The analogy is borne out by the fact that mercuric salts which do not hydrolyze do not give the reaction. Thus the mercuric halides give no reaction in many cases in which the acetate reacts with the greatest ease. Since the mercuric salts of all of the oxygen acids are considerably hydrolyzed they would be expected to act like the acetate with organic substances. Such is the case. The acetate, however, gives the best results.

The mercuration of a given aromatic compound by mercuric acetate follows practically the same course as the bromination of the same compound. Benzene can be mercurated under pressure at 110° and one, two, or even more acetoxymercuri groups may be introduced.

$$C_6H_6 + Hg(OAc)_2 \rightarrow C_6H_5 - HgOAc + HOAc.$$

Toluene is mercurated by refluxing with mercuric acetate. The product is a mixture of the o- and p- ring substituted compounds. In this case the analogy to bromination fails as it is impossible to obtain benzyl mercury compounds directly from toluene. This may be due to the great instability of these compounds. A case in which the mercuration takes exactly the same course as the corresponding bromination is presented by acetophenone which readily gives a phenacyl mercuric salt.

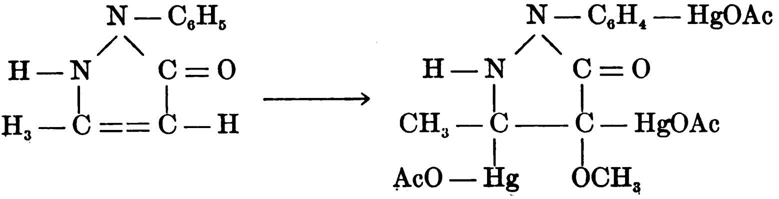
The groups which render bromination easy have the same effect on mercuration. As a rule, however, fewer mercury atoms than bromine atoms can be introduced into a given compound. Thus aniline gives o- and p- and di-mercurated compounds. Phenol gives a similar result. Just as nitrobenzene is harder to brominate than benzene it is harder to mercurate. Its reaction with mercuric acetate introduces us to an unexplained anomaly of mercuration—the mercury is never known to go in the meta position to the orienting group. Nitrobenzene gives an o-mercurated nitrobenzene. The mercuration of benzoic acid also gives an ortho compound. The best method for making mercurated benzoic acid is to heat ordinary mercuric benzoate to a high temperature. Benzoic acid is liberated. The residual mercury compound was long believed to be basic mercuric benzoate. In reality it is a $C - Hg$ compound having the mercury ortho to the carboxyl group. In this process the mercuric benzoate plays the part of mercurating agent and substance to be mercurated.



The product is the inner salt or anhydride of o-hydroxymercuribenzoic acid. Mercuration experiments have been performed with practically all of the available substituted anilines, phenols, and aromatic acids. Naphthalene is mercurated in the alpha position by mercuric acetate. Anthracene and phenanthrene also give the reaction but the products have not been studied.

Thiophene reacts easily with mercuric chloride in the presence of sodium acetate giving α-thienyl mercuric chloride. Refluxing commercial benzene with mercuric acetate yields an αα′-dimercurated thiophene without forming more than a trace of mercurated benzene. Substituted thiophenes are mercurated without any difficulty if at least one alpha position is open. If both alpha positions are substituted mercuration becomes more difficult. It is, however, possible to introduce mercury into one of the beta positions. The reaction then gives an intermediate compound which contains the groups — HgX and — OH, apparently added to one of the double bonds of the thiophene ring. Only long boiling eliminates a molecule of water leaving a substitution product having the — HgX group in the beta position. The formation of the intermediate addition compound in this case suggests the possibility that all aromatic compounds are mercurated by some such mechanism, the addition compounds losing water so readily that they cannot be isolated.

A number of phenyl-5-pyrazolones have been mercurated by mercuric acetate. Three or four mercury atoms are introduced into the molecule. Part of these go in the benzene nucleus and the rest in the pyrazolone ring. A typical example is the action of mercuric acetate in *cold* methyl alcohol on 3-methyl-1-phenyl-5-pyrazolone.



The resulting product, 1-acetoxymercuriphenyl-3-methyl-3, 4-di-acetoxymercuri-4-methoxy-3, 4-dihydro-5-pyrazolone, represents three different types of mercuration. The mercury on the phenyl groups enters the same as in aniline. The mercury attached to position 4 has replaced the alpha hydrogen originally there. The mercury in position 3 was added to the double bond with the methoxy group which is now attached to position 4. The study of other 5-pyrazolones has produced facts of interest in the general theory of substitution in organic compounds. Thus if no hydrogen is present in position 4 (alpha to the carbonyl group) mercuration becomes impossible except at elevated temperatures. If the pyrazolone has a phenyl group attached to the carbon in position 3 instead of to the nitrogen in position 1 it is still possible to mercurate the benzene nucleus, provided there is a hydrogen in position 4. This intimate relation of the hydrogen alpha to the carbonyl group in the pyrazolone ring to the mercuration of the benzene nucleus is decidedly interesting.

VI. Replacement of Acid Groups by Mercury.

The last method of mercuration to be considered is the replacement of acid groups in certain aromatic compounds by mercury. When the aromatic boric acids and sulfinic acids are heated with mercuric chloride solution the —HgCl group takes the place of the acid group.

$$C_6H_5-B(OH)_2 + HgCl_2 + H_2O \rightarrow C_6H_5-HgCl + HCl + H_3BO_3$$
$$C_6H_5-SO_2H + HgCl_2 \rightarrow C_6H_5-HgCl + SO_2 + HCl.$$

A process very much like these two is the action of an aromatic arsenious oxide with mercuric oxide.[5]

$$2R-AsO + 8NaOH + HgCl_2 \rightarrow R-Hg-R + 2NaCl + 2Na_3AsO_3 + 4H_2O.$$

A modification of these processes is the elimination of carbon dioxide from certain mercuric salts by heating.[6] Acids which lose carbon dioxide readily yield salts which have a similar instability. This process is applicable to both aliphatic and aromatic compounds. It may be illustrated by the general equation,

$$(R-CO_2)_2Hg \text{ heated} \rightarrow 2CO_2 + R_2Hg.$$

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[5] *Chem. Zentr.* 1914 I 1469. *D. R. P.* 272, 289.

[6] Private communication, M. S. Kharasch.

Chapter III.

General Properties and Reactions of Organic Mercury Compounds.

The important general reactions of these substances may be classified under the following headings:

(a) the action of acids, (b) the action of bases, (c) the action of sulfides, (d) the change from compounds of the type, $R - Hg - X$, to those of the type, R_2Hg, (e) the reverse of this change, that is, from R_2Hg to $R - Hg - X$, (f) the action of halogens, (g) the action of halides and cyanides of metals, (h) the action of halides of non-metals, (i) the action of alkyl and aryl halides, (j) the action of acid halides, and (k) the action of metals. In the next few paragraphs the general results of these reactions will be very briefly outlined. Then each of the eleven reactions will be considered in some detail. However, the treatment will not be exhaustive. Only a few typical examples and the cases of unusual interest will be considered under each reaction. Further examples and less general reactions will be found in the later chapters of the monograph.

The organic compounds of mercury differ radically from all other compounds having a metal attached to carbon. The linkage of mercury to carbon is capable of much greater stability than that of any other metal. Mercury compounds of the type of methyl mercuric iodide, $CH_3 - Hg - I$, resemble the Grignard reagent in formula only. They differ from the magnesium compounds in not being sensitive to active hydrogen compounds such as water, amines, and alcohols. It is true that they are attacked by acids giving the corresponding hydrocarbons, but this action generally takes place only with hot concentrated halogen acids. Moreover the organomercuric halides give no reaction with carbonyl compounds. The organic compounds in which both bonds of the mercury are attached to organic residues also differ from the corresponding compounds of other metals such as the zinc alkyls, the mercury compounds being stable to air and fairly stable to acids.

The mercury in most organic mercury compounds shows none of the reactions of ionized mercury. Potassium iodide does not form mercuric iodide except in some cases in which it reacts with an organomercuric iodide forming a mercury compound having both bonds attached to carbon and liberating one-half of the mercury in inorganic form. This reaction may be illustrated by the following equation,

$$2R - Hg - I + 2KI \rightarrow R_2Hg + K_2HgI_4.$$

Solutions of strong bases do not form mercuric oxide. They do not, as a rule, react with the organomercuric salts as these are salts of rather strong bases, the organomercuric hydroxides. Thus many organomercuric iodides can be recrystallized unchanged from hot alkali. In a very few cases compounds of the type $R - Hg - R$ react with solutions of bases giving substances, $R - Hg - OH$. Such a splitting of the $C - Hg$ linkage is very rare indeed.[1] The action of sulfides is the most sensitive indicator for mercuric ions, because of the extreme insolubility of mercuric sulfide. It is often said that mercury attached to carbon gives no mercuric sulfide when treated with hydrogen sulfide or ammonium sulfide. In reality, the formation of mercuric sulfide is usually rather slow, but it should be remembered that the stability of the $C - Hg$ linkage varies over the widest range, from compounds which give mercuric sulfide almost instantly, to those which do not give it even after long boiling with concentrated hydrochloric acid. No careful study has even been made of the relation between the constitution of organic mercury compounds and the ease with which they form mercuric sulfide. In cases in which mercuric sulfide is not formed immediately, an organomercuric sulfide is formed. This, on standing or heating, loses mercuric sulfide leaving an organic mercury compound, having both bonds of mercury attached to carbon. These reactions may be illustrated by the following equations,

$$2R - Hg - X + H_2S \rightarrow (R - Hg -)_2S + 2HX$$
$$(R - Hg -)_2S \text{ heated } \rightarrow R_2Hg + HgS.$$

The change from the organic mercury compounds of the type $R - Hg - X$ to the organic compounds, R_2Hg is one of the important general reactions of these substances. The reagents which bring about the change are most varied. Besides the inorganic iodides and sulfides just mentioned they are sodium thiosulfate, sodium stannite and

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[1] Whitmore and Middleton, *J. Am. Chem. Soc.* 43 (1921), 622.

various other alkaline reducing agents, potassium cyanide, potassium sulfocyanate and various metals such as sodium and copper. The various processes may be illustrated as follows,

$$2RHgI + 2KI \rightarrow R_2Hg + K_2HgI_4.$$
$$2RHgX + Na_2S \rightarrow (RHg)_2S \rightarrow R_2Hg + HgS.$$
$$2RHgX + 2Na_2S_2O_3 \rightarrow 2RHgS_2O_3Na \rightarrow R_2Hg + Na_2Hg(S_2O_3)_2.$$
$$2RHgX + Na_2SnO_2 + H_2O \rightarrow R_2Hg + Hg + 2NaX + Na_2SnO_3.$$
$$2RHgX + 2NaOH + 2Fe(OH)_2 \rightarrow R_2Hg + Hg + 2Fe(OH)_3.$$
$$2RHgCN + 2KCN \rightarrow R_2Hg + K_2Hg(CN)_4.$$
$$2RHgSCN + 2KSCN \rightarrow R_2Hg + K_2Hg(SCN)_4.$$
$$2RHgX + 2Na \rightarrow R_2Hg + Hg + 2NaX.$$

In each of these processes one-half of the mercury appears as inorganic mercury and the other half remains in the compound R_2Hg. No one of these reagents works satisfactorily with all kinds of organomercuric salts. The data on this reaction in the literature are entirely unsatisfactory.

The reverse of the above change is also an important reaction of organic mercury compounds.

$$R_2Hg + HgX_2 \rightarrow 2RHgX.$$

In this instance there are practically no complications. In almost every case a substance of the type R_2Hg will react quantitatively with a mercuric halide giving two molecules of the compound $R—Hg—X$. The reaction is brought about by mixing the substances in alcohol and boiling if necessary. It may be extended to mercury salts of other monobasic acids but apparently has never been completed with a mercury salt of a dibasic acid.

Organic mercury compounds react readily with halogens, giving products in which the position originally occupied by mercury is occupied by the halogen. Compounds of the type R_2Hg give two reactions, depending on the amount of halogen used. If only one molecule of the latter is used the products are $R—X$ and $R—Hg—X$. If an excess of halogen is used the organomercuric halide reacts further, giving another molecule of $R—X$ and a molecule of a mercuric halide. This reaction is useful in determining the structure of an organic mercury compound by changing it to a known halogen compound.

The only reaction in which the organic compounds of mercury resemble those of magnesium and zinc is their action with the halides of various non-metals such as boron, phosphorus, and arsenic. The reaction with these substances results in the formation of an organomercuric halide or an inorganic mercuric halide and a substance containing the organic residue in place of one or more of the halogen atoms of the halide. Thus phosphorus trichloride and mercury diphenyl easily give phenyl mercuric chloride and phenyl dichlorophosphine. A related set of reactions in which the mercury compounds fail to give the expected products is that involving organic halides. Organic mercury compounds very seldom react with alkyl halides or acyl halides to give the hydrocarbons or ketones which would be formed from the same halides by means of a Grignard reagent or a zinc alkyl.

The organomercuric halides give double decomposition reactions much like those of inorganic halides. Thus they act with silver salts and silver oxide, giving the corresponding organomercuric salts and hydroxides.[2] Phenyl mercuric halides have been treated with the acetate, nitrate, carbonate, and oxide of silver. The organomercuric halides do not react with sodium derivatives such as those of malonic ester and acetoacetic ester.

I. Reaction with Acids.

The linkage between carbon and mercury is usually fairly stable to dilute acids. Of the two possible types of compounds, those with both valences of mercury attached to carbon are more easily attacked by acids. Compounds of this type are easily split by both inorganic and organic acids, giving a hydrocarbon and an organomercuric salt.

$$(CH_3)_2Hg + HCl \rightarrow CH_3HgCl + CH_4.$$

Compounds having only one bond of the mercury attached to carbon react less readily with acids. Inorganic acids at high temperature will usually split these compounds but organic acids give little or no action unless heated to a high temperature under pressure. The action of an inorganic acid may be illustrated by the equation,

$$CH_3HgCl + HCl \rightarrow CH_4 + HgCl_2.$$

The stability of the carbon mercury linkage varies over the widest range. Thus substances having mercury alpha to a ketone group may lose the mercury on treatment with cold .25 normal hydrochloric acid while other substances, such as some of the mercarbides, are unchanged even after long heating with fuming hydrochloric acid. Al-

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[2] Otto, *J. prakt. Chem.* (2) 1 (1870), 180. *Ann.* 147 (1869), 164. Cahours, *J. prakt. Chem.* (2) 8 (1873), 398. *Comp. rend.* 77 (1873), 1403.

though almost all organic mercury compounds have been tested for their action with acids, the examples taken up in the following paragraphs will deal only with extreme cases or those of special interest.

Mercury diethyl heated in a sealed tube with glacial acetic acid at 190° gives an amount of ethane corresponding to one ethyl group. A small amount of ethylene is formed. Ninety-two per cent. of the mercury in the substance is recovered as metallic mercury. The other product is ethyl acetate which is obtained in a yield corresponding to 36% of the amount to be expected if all of the second ethyl group were changed to ethyl alcohol.[3] The reaction probably takes place in the following steps.

$$(C_2H_5)_2Hg + HOAc \rightarrow C_2H_6 + C_2H_5 - Hg - OAc.$$
$$C_2H_5 - Hg - OAc \rightarrow Hg + C_2H_5 - OAc.$$

The last step is a thermal decomposition which involves an intramolecular oxidation and reduction. In terms of the electronic conception of valence this would mean that at the moment of decomposition the mercury in the methylmercuric acetate no longer has two positive charges but has one positive and one negative charge, thus, $\overset{+-}{Hg}$. Such a molecule would be likely to lose free mercury readily, leaving the ethyl and acetate groups to combine with each other. Similar results have been obtained with mercury di-isoamyl and mercury dibenzyl.[4]

Iodomethylmercuric iodide, $ICH_2 - HgI$, when heated with hydrochloric acid gives methyl mercuric iodide.[5] If this observation is not due to some error it represents a most unusual replacement of an iodine atom by hydrogen.

The product from the action of acetylene with mercuric chloride (trichloromercuriacetaldehyde?) reacts with cold dilute hydrochloric acid forming acetaldehyde, mercuric chloride, and a trace of mercurous chloride.[6]

As has been mentioned, the C — Hg linkage in the mercarbides is unusually stable to acids. Ethane hexamercarbide, $C_2Hg_6O_2(OH)_2$, reacts with cold 10% hydrochloric acid, forming the salt $C_2Hg_6O_2Cl_2$. When this is heated for a long time with concentrated hydrochloric

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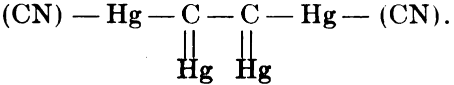
[3] Jones and Werner, *J. Am. Chem. Soc.* 40 (1918), 1270.

[4] *J. Am. Chem. Soc.* 40 (1918), 1270.

[5] Sakurai, *J. Chem. Soc.* 39 (1881), 489.

[6] Hofmann, *Ber.* 37 (1904), 4460. Brame, *J. Chem. Soc.* 87 (1905), 430.

acid it gives $C_2Hg_6Cl_6$. This substance is not changed by several days' boiling with concentrated hydrochloric acid.[7]

Another product obtained from ethane hexamercarbide is the complex cyanide,  $(CN)-Hg-\underset{\underset{Hg}{\|}}{C}-\underset{\underset{Hg}{\|}}{C}-Hg-(CN)$. Treatment of this substance with 10% hydrochloric acid gives hydrocyanic acid but no inorganic mercury. The product is a white powder having the formula $(ClHg)_2CH-CH(HgCl)_2$. When this compound is boiled with concentrated hydrochloric acid one-half of the mercury is changed to mercuric chloride and the rest remains in a volatile compound, $ClHg-CH_2-CH_2-HgCl$. The stability of this last compound to acid is shown by the fact that it can be distilled unchanged with concentrated hydrochloric acid.[8]

Mercury diphenyl reacts with dry hydrogen chloride gas, with evolution of heat, giving benzene and mercuric chloride. Moderate treatment with concentrated hydrochloric acid gives phenyl mercuric chloride. Nitric acid even at —15° acts violently with mercury diphenyl, giving mercuric nitrate and nitrobenzene.[9]

Mercury diphenyl dissolves easily in hot organic acids. When the mixture is diluted with water an organomercuric salt is precipitated. This is the method for making the formate, acetate and higher organic salts.[10]

Mercury diphenyl reacts with N-bromoacetamide forming phenyl mercuric bromide, benzene, and methyl isocyanate. The reaction thus consists in the action of mercury diphenyl on the hydrobromic acid split from the bromoamide.[11]

The three isomeric nitrophenylmercuric chlorides react with boiling hydrochloric acid giving nitrobenzene and mercuric chloride. The ortho and para compounds give this reaction more readily than the meta compound.[12]

Mercury bis-diphenyl, $(C_6H_5-C_6H_4-)_2Hg$, is not changed even by long boiling with concentrated hydrochloric acid.[13]

The phenol and naphthol mercuric salts are unusually sensitive to

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[7] Hofmann, *Ber.* 31 (1898), 1905; 33 (1900), 1336.

[8] Hofmann, *Ber.* 33 (1900), 1338.

[9] Dreher and Otto, *Ber.* 2 (1869), 543. *Ann.* 154 (1870), 97 ff.

[10] Otto, *J. prakt. Chem.* (2) 1 (1870), 185. Cf. *Ann.* 147 (1870), 164.

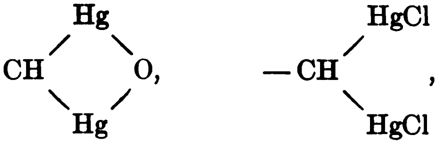
[11] Kharasch, *J. Am. Chem. Soc.* 43 (1921), May ?.

[12] Kharasch and Chalkley, *J. Am. Chem. Soc.* 43 (1921), 612.

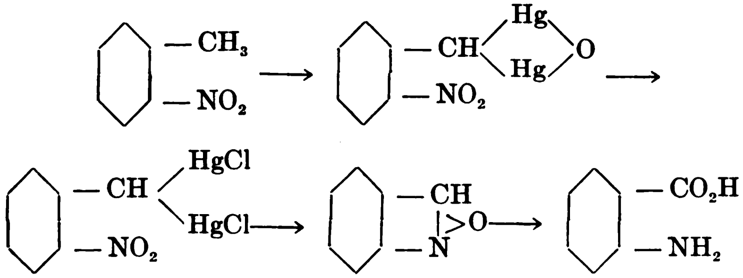
[13] Michaelis, *Ber.* 28 (1895), 592.

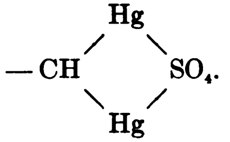
dilute mineral acids. The activity of the mercury in these compounds is almost as great as that of mercury in the alpha position to a carbonyl group.[14]

Phenacyl mercuric chloride, $C_6H_5 - CO - CH_2 - HgCl$, is decomposed readily by warm dilute hydrochloric acid.[15]

The compounds obtained from the nitrotoluenes and mercuric oxide give interesting results with acids. These substances have two mercury groups in the side chain,  , etc.

The compound from o-nitrotoluene reacts with cold concentrated hydrochloric acid giving anthranil which will react with sodium hydroxide giving the sodium salt of anthranilic acid. This series of changes from o-nitrotoluene to anthranilic acid represents an interesting intramolecular oxidation and reduction.[16]



These mercurated nitrotoluenes give a good illustration of the different splitting effects of halogen acids and oxygen acids on the C — Hg linkage. 10 to 20 per cent sulfuric acid acts on the complex oxides giving stable sulfates containing the grouping, . Halogen acids remove the mercury entirely.[16a]

The mercury compound obtained from 2, 4-dinitrotoluene reacts

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[14] Dimroth, *Ber.* 31 (1898), 2155. Bamberger, *Ber.* 31 (1898), 2625.

[15] Dimroth, *Ber.* 35 (1902), 2870.

[16] Reissert, *Ber.* 40 (1907), 4222.

[16a] *Ibid.* 4218.

with nitric acid of sp. gr. 1.4 forming 2, 4-dinitrobenzoic acid. This seems remarkable when it is recalled that dinitrotoluene must be heated for days at 100° with fuming nitric acid to change it to the dinitrobenzoic acid.[16b]

Tetrachloromercuri diphenylamine, $NH[C_6H_3(HgCl)_2]_2$, reacts with a mixture of fairly concentrated nitric acid and sulfuric acid to form a substance having two nitro groups but only three —HgCl groups. The position of these groups has not been determined.[17]

Thiophene mercuric chloride reacts readily with hydrochloric acid, giving thiophene and mercuric chloride.[18]

The iodomercuri compound of camphor $(C_{10}H_{14}O)_3Hg_4I_2$, reacts with halogen acids or hydrochloric acid giving mercuric salts and camphor. Dilute oxygen acids give no action. Concentrated nitric acid gives camphoric acid.

In mercurated 5-pyrazolones only the mercury in the 4 position (alpha to the carbonyl group) is easily removed by dilute hydrochloric acid. Thus 1-(diacetoxymercuriphenyl)-2, 3, dimethyl-3, 4 diacetoxymercuri-4-methoxy-3, 4-dihydro-5-pyrazolone when shaken for 12 hours with cold .25 normal hydrochloric acid, loses only the mercury in position 4, the other three mercury atoms remaining in the molecule. Similar results are given by other 5-pyrazolones.[19]

One compound having mercury in the alpha position is reported to be rather stable to acids. Bromomercuri acetic acid, $BrHg—CH_2—CO_2H$, is not decomposed by 20% nitric acid or dilute hydrochloric acid.[20]

The most remarkable reaction of acids with organic mercury compounds is the action with the "addition compounds" obtained from unsaturated compounds and mercuric salts. These substances may be divided into three classes which will be illustrated by the products obtainable from ethylene. Ethylene reacting with mercuric salts in water solution gives two types of compounds, $XHg—CH_2.CH_2OH$ and $XHg—CH_2.CH_2.O.CH_2.CH_2—HgX$. These may be referred to as the alcohol and ether derivatives respectively. If the reaction is carried out in alcohol solution an alkoxyl group is added instead of the hydroxyl in the first type of compound. Thus a methyl alcohol solu-

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[16b] *Ibid.* 4215.

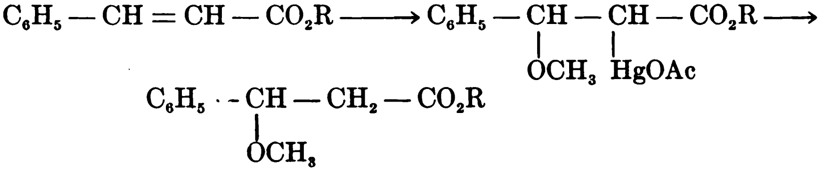
[17] Kharasch and Piccard, *J. Am. Chem. Soc.* 42 (1920), 1863.

[18] Volhard, *Ann.* 267 (1892), 174.

[19] Schrauth and Bauerschmidt, *Ber.* 47 (1914), 2740,

[20] Hofmann and Sand, *Ber.* 33 (1900), 1346.

tion gives $XHg-CH_2.CH_2.O.CH_3$ which may be referred to as a mixed ether derivative. The products to be expected from the action of acid on these substances would be ethyl alcohol, diethyl ether, and methyl ethyl ether. Such products are not obtained. The sole product of the action of hydrochloric acid on all three is ethylene. In general when an ethylene compound reacts with mercury salts the product will react with halogen acids giving back the original unsaturated compound. Corresponding results have been obtained with the higher olefines, with carbon monoxide, with allyl alcohol and with unsaturated acids and their esters, with terpineol, and with various allyl phenol derivatives. If the mercurated products really have the structures indicated, it appears that oxygen in the grouping $-O-C-C-Hg-$ must have a peculiar reactivity towards acids, or that the change of alcohols and ethers to olefines is possible by the action of acids in presence of mercury salts. Neither of these possibilities has received any experimental study. This peculiar reaction naturally lead some chemists to discard the structural formulas and assume certain molecular formulas such as $C_2H_4.Hg(OH)X$. As has been already stated, this type of formula would explain the action of acids, but it would not explain many of the other reactions of these compounds. Thus it is possible to change the "alcohol" compounds into ethyl alcohol by sulfides and into iodohydrine by iodine. The "ether" compound reacts with iodine giving the corresponding di-iododiethyl ether. The cinnamic ester compound obtained by the action of a methyl alcohol solution of mercuric acetate reacts with ammonium sulfide giving methoxy hydrocinnamic ester.



$$C_6H_5-CH=CH-CO_2R \longrightarrow C_6H_5-\underset{OCH_3}{\underset{|}{CH}}-\underset{HgOAc}{\underset{|}{CH}}-CO_2R \longrightarrow$$

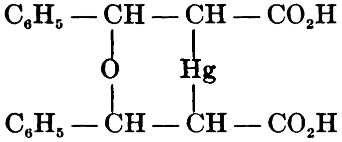
$$C_6H_5-\underset{OCH_3}{\underset{|}{CH}}-CH_2-CO_2R$$

If the mercury product is regarded as a "molecular" compound without any structural relations between the added group and the unsaturated carbons, then it must be assumed that the action of the sulfide causes a molecule of methyl alcohol to add to the double bond of the cinnamic ester.

The reaction of acids with the mercury compounds of acetylene can hardly be understood until the true nature of these mercury compounds is settled. As has been stated, the treatment with acids in most cases gives a hydration product of the original acetylene. In some cases, however, this product is accompanied by some of the original acetylene. Such is the case with the mercury compound of phenyl acetylene.[21]

The reaction product of dihydronaphthalene and mercuric acetate, which has —HgX and —OH added to the 2, 3 carbon atoms, reacts with cold 30% hydrochloric acid giving pure dihydronaphthalene.[22]

A remarkably stable compound of the "ether" type is the product of the action of potassium iodide on the anhydride of α-hydroxymercuri β-methoxy hydrocinnamic acid. This product is formulated as



$$\begin{array}{l} C_6H_5 - CH - CH - CO_2H \\ \qquad\quad | \qquad\;\; | \\ \qquad\quad O \qquad Hg \\ \qquad\quad | \qquad\;\; | \\ C_6H_5 - CH - CH - CO_2H \end{array}$$

It gives no mercuric ions except on long boiling with concentrated nitric or hydrochloric acids.[23]

II. Reaction with Bases.

Bases as a general rule do not break the carbon mercury linkage. No case is known in which a true organic mercury compound gives mercuric oxide when treated with a base. The one case in which alkali breaks the linkage C — Hg is that of the mercurated phenols. An acetylated mercury diphenol, $(AcO - C_6H_4 -)_2Hg$, when saponified by sodium hydroxide does not give the expected mercury diphenol, $(HO - C_6H_4 -)_2Hg$, but instead gives a compound having only one bond of the mercury attached to a benzene nucleus and the other attached to oxygen.[24]

Many organic mercury compounds dissolve in solutions of bases and can be recovered unchanged by cooling or by cautious treatment with acid. Thus the mercurated anilines are soluble in ammonium hydroxide and can be recovered by treatment with acetic acid. In this case the solubility is probably due to the formation of a com-

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[21] Manchot and Haas, *Ann.* 399 (1913), 138.

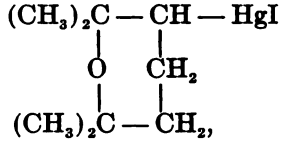
[22] Sand and Genssler, *Ber.* 36 (1903), 3699.

[23] Schoeller, Schrauth, and Struensee, *Ber.* 44 (1911), 1057.

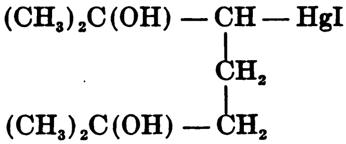
[24] Whitmore and Middleton, *J. Am. Chem. Soc.* 43 (1921), 622. A similar reaction has been noted with 5-Mercury-bis-3-nitro-4-hydroxyphenyl arsonic acid which changes to a compound having only one organic residue attached to mercury on standing with alkali. Stieglitz, Kharasch, and Hanke, *J. Am. Chem. Soc.* 43 (1921), May ?,

pound between the ammonia and the mercurated amine. Other inorganic bases do not give the same results.[25]

Almost all of the compounds formed from unsaturated substances and mercuric salts are soluble in sodium hydroxide solution. The acetates, chlorides and bromides are usually soluble cold and can be recovered only by careful acidification or better by saturating the basic solution with carbon dioxide. The iodides are usually soluble only on heating and crystallize out on cooling.[26] The "ether" compounds are usually less soluble in bases than the "alcohol" compounds. This fact may be illustrated by means of the two compounds obtained by adding — HgX and — OH to dimethylheptenol. The "ether" compound,

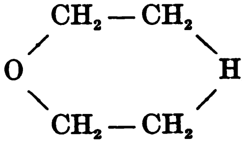


is completely insoluble in concentrated KOH, while the "alcohol" compound



$$\begin{array}{ll}(CH_3)_2C(OH) - & CH - HgI \\ & \vert \\ & CH_2 \\ & \vert \\ (CH_3)_2C(OH) - & CH_2\end{array}$$

is soluble. Similar relations hold with cineol mercuric iodide and trans-terpinol mercuric iodide obtained by addition to the double bond of terpineol.[27]

The compounds which have both bonds of mercury attached to carbon are usually not soluble in bases. Thus, although the compound, $O(CH_2 - CH_2 - HgBr)_2$, is readily soluble in bases, the corresponding compound, , obtained from it by alkaline sodium stannite solution, is entirely insoluble in sodium hydroxide.[28]

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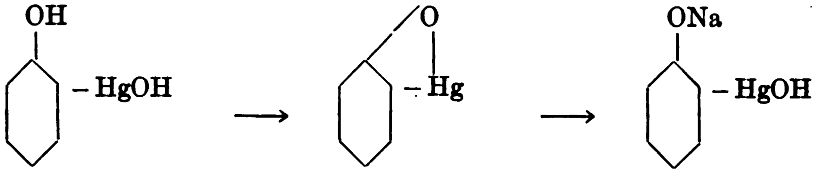
[25] Vecchiotti, *Gazz. chim. ital.* 48 II (1918), 80. *Chem. Abst.* 13 (1919), 1450.

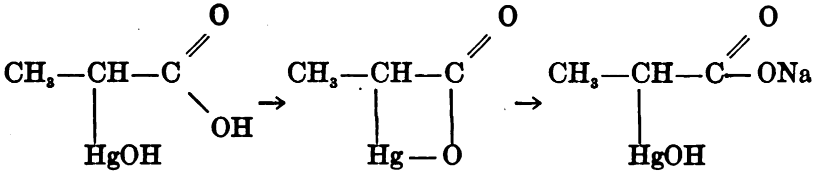
[26] Hofmann and Sand, *Ber.* 33 (1900), 2694. Sand, *Ber.* 34 (1901), 1391. Sand and Genssler, *Ber.* 36 (1903), 3705.

[27] Sand and Singer, *Ber.* 35 (1902), 3174.

[28] Sand, *Ber.* 34 (1901), 2913.

Mercury compounds containing free phenol or carboxyl groups are, of course, soluble in bases. Many mercury compounds of these two types readily form anhydrides or inner salts which are insoluble in water. These anhydro compounds readily dissolve in alkalies, giving solutions of the corresponding salts. These changes may be illustrated by the following:





Unstable. Insoluble. Soluble.

The compounds of the nitrotoluenes having mercury in the side chain are stable to dilute alkalies but react on long boiling with concentrated alkalies giving dark decomposition products, which have not been studied.

An unusually interesting reaction of bases with organic mercury compounds is the action of sodium hydroxide on the product of carbon monoxide and a methyl alcohol solution of mercuric acetate. This substance is formulated as acetoxymercuri formic methyl ester, $AcO — Hg — CO_2CH_3$. It dissolves in sodium hydroxide giving a clear solution which gradually deposits metallic mercury. The solution is then found to contain a carbonate. Apparently the molecule $HO — Hg — CO_2Na$ is very unstable and readily undergoes intramolecular oxidation and reduction giving mercury and sodium bicarbonate.[29]

A similar result is obtained on the addition of bases to iodomethylmercuric iodide. Metallic mercury is formed at once. If the iodide is treated with a suspension of silver oxide, a water solution is obtained which deposits metallic mercury on standing.[30]

[29] Schoeller and Schrauth, *Ber.* 46 (1913), 2871.
[30] Whitmore and Middleton, unpublished results.

This case resembles that of the formate in that the unstable product contains mercury attached to a carbon bearing a hydroxyl group. Apparently such a grouping is very unstable.

III. Reaction with Sulfides.

As has been indicated the stability of organic mercury compounds to sulfides varies over wide limits. If mercuric sulfide is not formed at once an organomercuric sulfide is obtained which decomposes more or less readily giving mercuric sulfide.

$$RHgX \longrightarrow (RHg)_2S \longrightarrow R_2Hg + HgS.$$

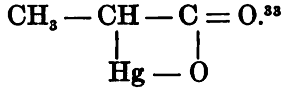
The compounds which give mercuric sulfide quite rapidly are those which have mercury in the alpha position to some group, like the carbonyl or phenyl, which renders an alpha halogen atom unusually reactive. Thus the bromine in bromoacetophenone is unusually reactive and the mercury in the same position is very readily removed by sulfides. Among the compounds which react almost instantly with sulfides are the following:—

(a) Allyl mercuric iodide, $CH_2 = CH - CH_2 - HgI$.[31]

(b) Sodium salt of hydroxymercuriacetic acid,

$$HO - Hg - CH_2CO_2Na.^{32}$$

(c) Anhydro hydroxymercuripropionic acid,



$$\begin{array}{l} CH_3 - CH - C = O.^{33} \\ \phantom{CH_3 - {}} | \phantom{{} - {}} | \\ \phantom{CH_3 - {}} Hg - O \end{array}$$

In marked contrast to this action of the alpha mercury compound is that of the corresponding beta mercurated compound which does not react with ammonium sulfide.[34]

(d) Mercury malonic ester,[35] $(RO_2C)_2CH - Hg - CH(CO_2R)_2$.

(e) Hydroxymercury methyl malonic ester,[36]

$$HO - Hg - C(CH_3)(CO_2R)_2.$$

(f) Hydroxymercuricyanacetic acid and its homologs.[37]

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[31] Linnemann, *Ann. Spl.* 3 (1865), 262.

[32] Schoeller and Schrauth, *Ber.* 41 (1908), 2091.

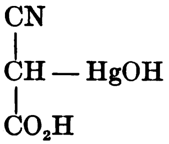
[33] Schoeller and Schrauth, *Ber.* 42 (1909), 783.

[34] *Ibid.* Schoeller, Schrauth, and Müller, *Biochem. Z.* 33 (1911), 401.

[35] Billmann, *Ber.* 35 (1902), 2582. Schoeller and Schrauth, *Ber.* 41 (1908), 2091. Schoeller, Schrauth, and Müller, loc. cit. 400.

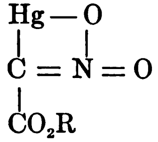
[36] Schoeller and Schrauth, loc. cit. 782.

[37] Petterson, *J. prakt. Chem.* (2) 86 (1912), 463.

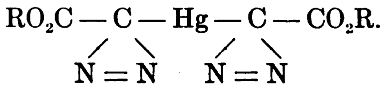


$$\begin{array}{l} CN \\ | \\ CH - HgOH \\ | \\ CO_2H \end{array}$$

(g) Anhydro hydroxymercurinitroacetic ester.[38]

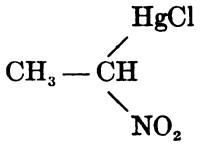


(h) Mercuribis-diazoacetic ester.[39]



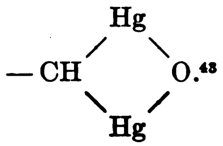
(i) "Tri-mercury diacetone hydrate." [40]

(j) Chloromercuri nitro ethane.[41]



(k) Phenacyl mercuric chloride.[42] $C_6H_5 - CO - CH_2 - HgCl$.

(l) Mercurated nitrotoluenes containing the grouping



(m) Mercurated 5-pyrazolones which have mercury in the 4 position, that is, alpha to the carbonyl group, have this mercury replaced by hydrogen when treated with ammonium sulfide. Mercury in other positions does not react readily with sulfides.[44]

As has been stated, organic mercury compounds often react with sulfides giving organomercuric sulfides of the type $(R - Hg)_2S$ which change more or less readily to HgS and R_2Hg or to RH and HgS in presence of an excess of the sulfide. Among the substances which behave in this way are the following:

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[38] Scholl and Nyberg, *Ber.* 39 (1906), 1957.

[39] Buchner, *Ber.* 28 (1895), 218.

[40] Auld and Hantzsch, *Ber.* 38 (1905), 2683

[41] Scholl and Nyberg, loc. cit. 1958.

[42] Dimroth, *Ber.* 35 (1902), 2870.

[43] Reissert, *Ber.* 40 (1907), 4211 ff.

[44] Schrauth and Bauerschmidt, *Ber.* 47 (1914), 2740.

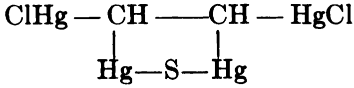
(a) Methyl mercuric salts.[45] The stability of the organic sulfide is shown by the fact that it can be made from a solution of methyl mercuric chloride in 10% hydrochloric acid.

(b) Ethyl mercuric chloride reacts with ammonium sulfide giving a yellowish precipitate of $(EtHg)_2S$. This precipitate is soluble in an excess of ammonium sulfide. Heating changes it to mercuric sulfide.[46]

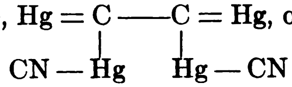
(c) n-Hexyl mercuric bromide dissolved in pyridine reacts with hydrogen sulfide at — 10° giving a white precipitate which is stable if kept dry and dark. If exposed to moisture it blackens in a few hours.[47]

(d) Pentamethylene di-mercuric bromide reacts with hydrogen sulfide in pyridine giving a rather stable sulfide. When the sulfide is dry it must be heated to 160° to change it to mercuric sulfide. When suspended in aniline or pyridine it blackens at 70°. However, the change to mercuric sulfide is not complete, even after heating the suspension at 175° for several days.[48]

Among the substances of greatest stability to sulfides are the mercarbides. This undoubtedly is partly due to their extreme insolubility. Ethane hexamercarbide is only partly decomposed even after boiling with hydrochloric acid and hydrogen sulfide for several days.[49] A white complex sulfide forms readily even at room temperature. The remarkable stability of the C — Hg linkages in this sulfide may be seen from the fact that treatment of the compound with chlorine water, nitric acid, and then with sodium hydroxide gives back the original mercarbide.[50] Treatment of the mercarbide with potassium polysulfide and then with hydrochloric acid gives a compound,



$$\begin{array}{ccccc} \mathrm{ClHg}- & \mathrm{CH} & - & \mathrm{CH} & -\mathrm{HgCl}. \\ & | & & | & \\ & \mathrm{Hg} & -\mathrm{S}- & \mathrm{Hg} & \end{array}$$ [51]

The mercarbide, 

$$\begin{array}{cccc} \mathrm{Hg}= & \mathrm{C} & - & \mathrm{C} = \mathrm{Hg} \\ & | & & | \\ \mathrm{CN}- & \mathrm{Hg} & & \mathrm{Hg}-\mathrm{CN} \end{array}$$

obtained from the hexamercar-

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[45] Frankland, *Ann.* 85 (1853), 363. Otto, *Ann.* 154 (1870), 199. Hilpert and Ditmar, *Ber.* 46 (1913), 3740.

[46] Dünhaupt, *J. prakt. Chem.* (1) 61 (1854), 426.

[47] Grüttner, *Ber.* 47 (1914), 1655.

[48] Hilpert and Grüttner, *Ber.* 47 (1914), 182.

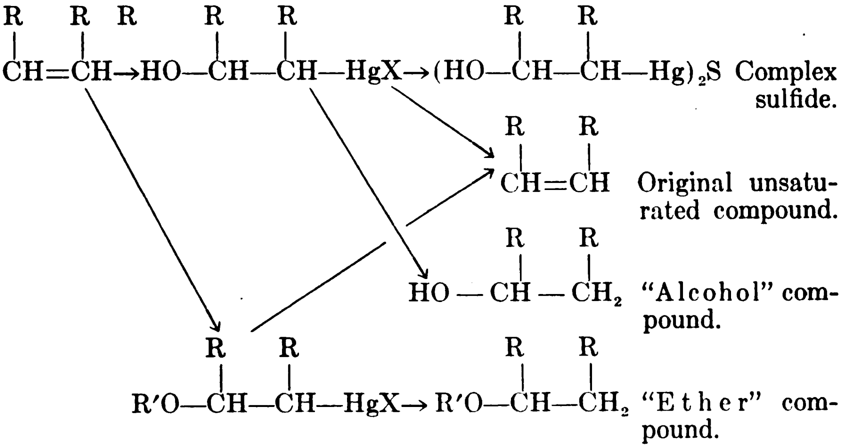
[49] Hofmann, *Ber.* 31 (1898), 1905.

[50] Hofmann, *Ber.* 33 (1900), 1337.

[51] Hofmann and Feigel, *Ber.* 38 (1905), 3657.

bide by treatment with potassium cyanide reacts with hydrogen sulfide in cold 15% nitric acid giving the corresponding —SH compound, $C_2Hg_4(SH)_2$.[52] Ethylene di-mercuric chloride, $ClHg—CH_2.CH_2—HgCl$, obtained from the cyanide just mentioned, reacts with hydrogen sulfide in hydrochloric acid solution giving a white sulfide which is insoluble in 20% cold nitric acid but can be recrystallized from hot alcohol.

The products formed from ethylene compounds and mercuric salts react with sulfides in three ways. Some give organomercuric sulfides of greater or less stability. Others give the original unsaturated compounds, and still others, under proper conditions, give compounds containing a molecule of water or alcohol added to the original double bond. These changes may be illustrated by the following,



This last type of reaction is of greatest interest as it throws light on the constitution of the mercury addition products. The best way to obtain this result is to dissolve the mercury compound in sodium hydroxide, if possible, and then pass in hydrogen sulfide in excess. The mercury sulfide held in solution by the alkaline sulfide is precipitated by adding an ammonium salt and the organic product is extracted from the filtered solution. If the mercury compound is not soluble in sodium hydroxide the same result may sometimes be obtained by dissolving it in alcohol and then passing in hydrogen sulfide and ammonia gas. The following compounds have been found to give this reaction:—

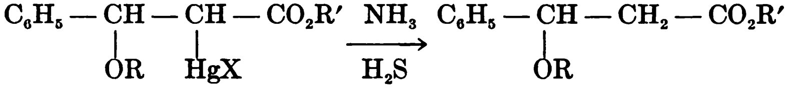
[52] Hofmann, *Ber.* 33 (1900), 1338.

(a) Anhydro α-hydroxymercuri β-hydroxybutyric acid obtained from crotonic acid when treated with sodium hydroxide and hydrogen sulfide gives β-hydroxybutyric acid. If the reaction is carried out in acid solution crotonic acid is the product.[53]

(b) The sodium salt of hydroxymercuri hydroxysuccinic acid obtained from maleic acid reacts with sodium hydroxide and hydrogen sulfide giving about 80% of the calculated amount of *malic acid.*[54]

(c) The anhydride obtained from allocinnamic acid and mercuric salts reacts with sodium hydroxide and hydrogen sulfide giving phenyl hydracrylic acid, $C_6H_5-CHOH-CH_2-CO_2H$. If the reaction is carried out in hot acid solution the product is common cinnamic acid.[55]

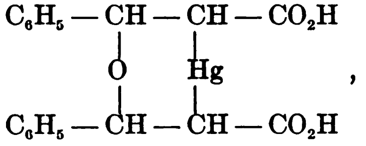
(d) The α-acetoxymercuri-β-alkoxyl hydrocinnamic esters obtained from cinnamic esters and mercuric acetate in various alcohols react with ammonia and hydrogen sulfide forming the corresponding β-alkoxyl hydrocinnamic esters.



$$C_6H_5-\underset{\displaystyle OR}{\underset{|}{CH}}-\underset{\displaystyle HgX}{\underset{|}{CH}}-CO_2R' \xrightarrow[H_2S]{NH_3} C_6H_5-\underset{\displaystyle OR}{\underset{|}{CH}}-CH_2-CO_2R'$$

The reaction has been carried out with alkoxyl derivatives of the following alcohols, methyl, ethyl, n-propyl, isopropyl and isobutyl.[56]

Mercury di-β-phenyl anhydrohydracrylic acid,



$$\begin{array}{ccccccc} C_6H_5 & - & CH & - & CH & - & CO_2H \\ & & | & & | & & \\ & & O & & Hg & & \\ & & | & & | & & \\ C_6H_5 & - & CH & - & CH & - & CO_2H \end{array},$$

obtained from the anhydro methoxy hydroxymercuri hydrocinnamic acid and potassium iodide is remarkably stable to sulfides. Its solution in ammonium hydroxide gives no mercuric sulfide even on long boiling with ammonium sulfide. Only after long boiling with concentrated hydrochloric acid or nitric acid will it give any action with sulfides.[57]

Most of the other products obtainable from ethylene compounds and mercuric salts have been found to act more or less readily with sulfides but little attempt has been made to identify the organic prod-

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[53] Biilmann, *Ber.* 35 (1902), 2576; 43 (1910), 579.
[54] *Ibid.* 577.
[55] *Ibid.*
[56] Schoeller, Schrauth, and Struensee, *Ber.* 43 (1910), 698; 44 (1911), 1432.
[57] Schoeller, Schrauth, and Struensee, *Ber.* 44 (1911), 1057.

ucts. Ethanol mercuric chloride in alkaline solution reacts with potassium sulfide giving a white precipitate of $(HO-CH_2.CH_2-Hg)_2S$ which, on boiling with water, is hydrolyzed to the corresponding sulfhydrate and hydroxide, without giving any mercuric sulfide.[58] Di-ethyl ether di-mercuric bromide in alkaline solution reacts with potassium sulfide giving a white precipitate which is insoluble in hot potassium hydroxide.[59]

Acetoxymercuriformic methyl ester obtained from carbon monoxide and a methyl alcohol solution of mercuric acetate reacts with a small amount of hydrogen sulfide in the cold giving a white sulfide which blackens on standing, heating, or treating with hydrochloric acid.[60]

Some of the mercury addition products obtained from allyl compounds such as safrol and the methyl ether of eugenol do not react with ammonium sulfide but are blackened by hydrogen sulfide. This phenomenon has not been explained.[61]

The compound, $C_{10}H_{16}O(HgOAc)_2$, obtained from camphene and mercuric acetate reacts slowly with hydrogen sulfide and dilute hydrochloric acid giving mercuric sulfide and camphene.[62]

The reaction of 5-pyrazolones having mercury in the 4-position, alpha to the carbonyl group, has been mentioned. Most of these mercurated pyrazolones also have mercury in the 3 position which was put there by addition of the groups — HgOAc and OCH_3 to the double bond between the 3 and 4 carbon atoms. This mercury is not attacked by sulfides as readily as the mercury in the 4 position. Long standing with ammonium sulfide is necessary to give mercuric sulfide.[63]

1-phenyl-3-methyl-4-acetoxymercuri-5-chloro pyrazoline is not blackened immediately by ammonium sulfide.[64]

Mercury acetylide reacts violently with ammonium sulfide giving mercuric sulfide and acetylene.[65] The product from mercuric chloride and acetylene is blackened at once by ammonium sulfide but gives only 1% of the acetylene used in its preparation.[66]

The mercury compounds of the trihalogen ethylenes and the mono-

[58] Hofmann and Sand, *Ber.* 33 (1900), 1350.

[59] *Ibid.*, 2695.

[60] Schoeller and Schrauth, *Ber.* 46 (1913), 2872.

[61] Balbiano and Nardacci, *Gazz. chim. ital.* 36 I (1906), 270. Manchot, *Ann.* 421 (1920), 320.

[62] Balbiano, *Ber.* 36 (1903), 3577. *Gazz. chim. ital.* loc. cit.

[63] Schrauth and Bauerschmidt, *Ber.* 47 (1914), 2740.

[64] *Ibid.*

[65] Manchot and Haas, *Ann.* 399 (1913), 152.

[66] Biltz and Reinkober, *Ann.* 404 (1914), 224.

halogen acetylenes react at once with ammonium sulfide.[67] The mercury compounds of phenyl acetylene do the same.[68]

The aromatic mercury compounds with the exception of the mercurated phenols are more stable to sulfides than the aliphatic compounds. Phenyl and tolyl mercuric salts form the organomercuric sulfides in the usual way. This is one important method of changing them to mercury diphenyl and mercury ditolyl. Long continued action of hydrogen sulfide changes all of the organic mercury to mercuric sulfide and leaves hydrocarbons.[69]

Many of the mercurated anilines react with barium sulfhydrate solution giving organic mercury sulfides which on heating give the mercury di-anilines. The reaction has been carried out with aniline, methyl aniline, dimethyl aniline, ethyl aniline, diethyl aniline and acetanilide.[70]

If the product of the action of the calculated amount of barium sulfhydrate[71] solution or dilute sodium sulfide solution is warmed with 50% sodium sulfide the mercury is entirely eliminated as mercuric sulfide.[72]

The mercurated phenols do not give mercuric sulfide at once on treatment with sulfides but the organic mercury sulfides formed decompose more readily than most aromatic compounds of this type.[73]

The mercurated nitrophenols do not give mercuric sulfide with ammonium sulfide or hydrogen sulfide.[74]

Mercury fluorescein dissolved in ammonium hydroxide and heated with ammonium sulfide gives mercuric sulfide.[75]

A careful study has been made of the speed with which ammonium sulfide blackens the sodium salts of various mercurated benzoic acids containing the group —HgOH. The time in minutes required for blackening the sodium salts is as follows: salicylic 14, anthranilic 20, sulfosalicylic 60, o-toluic 145, o-iodobenzoic 170, o-chlorobenzoic 255, benzoic 540. The greater stability of the compounds having both

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[67] Hofmann and Kirmreuther, *Ber.* 41 (1908), 315; 42 (1909), 4235.

[68] Manchot and Haas, loc. cit. 138 ff.

[69] Dreher and Otto, *Ann.* 154 (1870), 116, 174. Otto, *J. prakt. Chem.* (2) 1 (1870), 182. Dreher and Otto, *Ber.* 2 (1869), 544.

[70] Pesci, *Gazz. chim. ital.* 29 I (1899), 394.

[71] Piccinini, *Gazz. chim. ital.* 23 II (1893), 537. Pesci, *Z. anorg. Chem.* 15 (1897), 217 ff. Dimroth, *Ber.* 35 (1902), 2044.

[72] Pesci, *Gazz. chim. ital.* 23 II (1893), 524.

[73] Dimroth, *Chem. Zentr.* 1901 I 451. *Ber.* 35 (1902), 2866.

[74] Hantzsch and Auld, *Ber.* 39 (1906), 1110.

[75] *D. R. P.* 308, 335. *Chem. Abst.* 13 (1919), 1621.

bonds of the mercury attached to aromatic residues is shown by the fact that the sodium salt of mercury dibenzoic acid is blackened only after three weeks standing with ammonium sulfide. Inorganic halide solutions exert a profound effect on the formation of mercuric sulfide from these compounds. The addition of a 5% solution of ammonium chloride cuts down the time required for blackening from 14 minutes to 2 minutes for the salicylic derivative and from 540 to 135 for the benzoic compound.[76]

The mercurated benzoic acids form organic mercuric sulfides which can be changed to the mercury dibenzoic acids by heating.[77] The corresponding acid chloride $(ClCO — C_6H_4 — Hg)_2S$, when boiled with methyl alcohol gives o-chloromercuribenzoic methyl ester, methyl benzoate, mercuric sulfide, and hydrochloric acid. In all probability the R_2Hg compound is formed here as usual but is split into RH and $R — Hg — Cl$ by the hydrochloric acid formed from the acid chloride and the alcohol.[78]

Similar complex sulfides have been made from mercurated aminobenzoic acids and their esters[79] and from mercurated salicylic acid and other hydroxybenzoic acids and esters.[80] *o*-Chloromercuribenzophenone reacts very slowly with hydrogen sulfide even when heated.[81] The carbinol obtained from the action of this mercurated ketone with ethyl magnesium bromide is even more stable to sulfides.[82]

An alcoholic solution of α-mercury dinaphthyl does not act with hydrogen sulfide.[83] α-Naphthyl mercuric acetate in alcohol reacts with sulfides giving a white precipitate. An excess of ammonium sulfide at 100° converts this to mercuric sulfide and naphthalene.[84]

Dimercurated α-naphthylamine reacts very slowly with ammonium sulfide.[85] The mercury derivatives of the sulfonic acids of α-naphthylamine show a similar behaviour.[86]

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[76] Schoeller, Schrauth, and Müller, *Biochem. Z.* 33 (1911), 403.

[77] Pesci, *Gazz. chim. ital.* 32 II (1902), 292; *Chem. Zentr.* 1902 II 1454. Schoeller and Schrauth, *Ber.* 53 (1920), 637.

[78] Sachs, *Ber.* 53 (1920), 1740.

[79] Blumenthal, *Biochem. Z.* 32 (1911), 60 ff. Schoeller and Hueter, *Ber.* 47 (1914), 1935. Schoeller, Schrauth, and Liese, *Ber.* 52 (1919), 1784.

[80] Rupp, *Arch. Pharm.* 239 (1901), 114; *Chem. Zentr.* 1901 I 972. Dimroth, *Ber.* 35 (1902), 2872. Schoeller, Schrauth, and Müller, *Biochem. Z.* 33 (1911), 400. *Chem. Abst.* 5 (1911), 3880. Schoeller and Schrauth, *Ber.* 53 (1920), 639.

[81] Dimroth, *Ber.* 35 (1902), 2868.

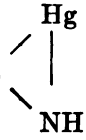
[82] Grignard and Abelmann, *Bull. soc. chim.* (4) 19 (1916), 25.

[83] Otto and Möries, *Ann.* 147 (1868), 171.

[84] Otto, *Ann.* 154 (1870), 191.

[85] Brieger and Schulemann, *J. prakt. Chem.* (2) 89 (1914), 141.

[86] *Ibid.* 151 ff.

Monomercurated β-naphthylamine is blackened instantly by ammonium sulfide.[87] The sodium salt of 1-hydroxymercuri-β-naphthylamine-6-sulfonic acid is obtained in two forms, a yellow anhydride apparently containing the grouping,  $\begin{array}{l} \diagup\,\text{Hg} \\ \quad | \\ \diagdown\,\text{NH} \end{array}$, which reacts instantly giving mercuric sulfide, and a hydrated colorless form which does not act with ammonium sulfide.[88]

α-Naphthol reacts with mercuric acetate giving a yellow gel which is blackened at once by ammonium sulfide. The corresponding hydroxide gives no action until it has stood with ammonium sulfide for a few minutes. The di-mercurated product from α-naphthol does not react with ammonium sulfide at all. The same is true of the mercurated α-naphthol-4-sulfonic acid.[89]

Mercury derivatives of β-naphthol and its sulfonic acids and carboxylic acids are very stable to ammonium sulfide. The addition of inorganic halides, especially iodides, hastens the formation of mercuric sulfide apparently by exerting a "loosening" action on the C — Hg linkage.[90]

The mercurated thiophenes in alcohol solution react with hydrogen sulfide giving mercuric sulfide.[91]

Tyrosin forms a mercury compound which is stable to hydrogen sulfide.[92] Mercury phenosafranine reacts with hot ammonium sulfide very slowly giving mercuric sulfide.[93]

The mercury derivatives of theobromine and theophylline do not act with ammonium sulfide.[94]

Various compounds of mercury salicylic acid are more stable to sulfides than the substance itself. Thus the sodium salt of mercurated salicylic acid is blackened in 14 minutes while its compound with sodium amino-oxyisobutyrate is blackened only after 30 minutes.[95] Even more remarkable substances are the water soluble compounds

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[87] Brieger and Schulemann, *J. prakt. Chem.* (2) 89 (1914), 141.
[88] *Ibid.* 145.
[89] *Ibid.* 135 ff.
[90] *Ibid.* 105 ff.
[91] Volhard, *Ann.* 267 (1892), 175.
[92] *D. R. P.* 267, 411. Fränkel, *Die Arzneimittelsynthese*, 1919, p. 661.
[93] *Chem. Zentr.* 1915 II 569.
[94] *D. R. P.* 282, 377. Fränkel, 676.
[95] Schoeller, Schrauth, and Müller, *Biochem. Z.* 33 (1911), 381.

obtained from mercury salicylic acid and the mercurated sulfamido benzoic acids. The latter compounds contain the group $—SO_2—NH—HgOH$ and react instantly with cold ammonium sulfide as do all N — Hg compounds. However their compounds with mercury salicylic acid give mercuric sulfide only on boiling with ammonium sulfide.

Recently the reactivity of a number of mercury derivatives of dihydroxy and amino hydroxy benzenes with sulfides has been studied.[96] It is found that if both groups are "protected" by methylation or acylation the substance does not act readily with sulfides. *Acetoxymercuriresorcinol* reacts at once with ammonium sulfide. *Diacetoxymercuriresorcinol dimethyl ether* is very stable to ammonium sulfide. *Acetoxymercuricatechol monomethyl ether* is fairly stable to sulfides. *Acetoxymercuri-m-hydroxy-dimethylaniline* reacts readily with ammonium sulfide. The corresponding *acetyl derivative* is stable to ammonium sulfide. *4, 4′-Mercuribis-(3-hydroxyphenyl-trimethyl-ammonium acetate)* is exceedingly stable to ammonium sulfide.

IV. Change of Compounds of the Type R-Hg-X to Those of the Type R-Hg-R.

In a few cases this change takes place spontaneously or on heating without the addition of any reagent. It may be represented by the equations

$$2RHgX = R_2Hg + HgX_2$$
$$(RHg)_2Y'' = R_2Hg + HgY''$$

in which X and Y are univalent and bivalent acid radicals. The only compounds of the first class which undergo the change without the addition of any reagent are the α-thiophene mercuric iodides. When an attempt is made to prepare these compounds in the usual way by treating the chloride with one molecule of sodium iodide a considerable amount of mercury dithienyl crystallizes out and a correspondingly smaller amount of the iodide is obtained from the mother liquors. To the second class of compounds belong the organomercuric sulfides and thiosulfates which decompose on heating. The length of time taken for this decomposition varies over a wide range. In most cases the best way to bring about the changes represented in these equations if they will not take place on heating is to add an excess of a substance which will remove HgX_2 or HgY either by changing them to metallic

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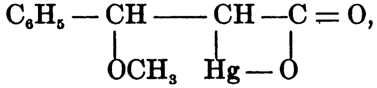
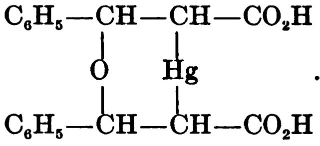
[96] Private communication, Kharasch and Chalkley.

mercury or to a complex mercuric ion. Even in those cases where heat alone will cause the change the addition of some such reagent hastens the reaction. Thus the change from an organomercuric thiosulfate to the R_2Hg compound is hastened by using an excess of concentrated sodium thiosulfate which forms sodium mercuric thiosulfate, $Na_2Hg(S_2O_3)_2$.

The iodides which have been found to change to the R_2Hg compounds on heating are α-thiophene mercuric iodide and α′-iodo-α-iodomercuri thiophene. The corresponding bromo and chloro compounds are changed to R_2Hg only by an excess of the iodide which removes the mercuric iodide as Na_2HgI_4. When the — HgI group is in the beta position the change to the R_2Hg compound does not take place spontaneously or even in presence of an excess of inorganic iodide. This change has been brought about only by the action of metallic sodium in boiling xylene.

In the case of some substituted anilines, the action of an excess of alcoholic sodium or potassium iodide is the best way to make the R_2Hg compound. Such a case is that of o-acetoxymercuri-p-bromodimethylaniline which gives an 86% yield of the mercury diphenyl derivative on refluxing for 8 hours with potassium iodide.[97] The theory that this action is due to a complex formation is strengthened by the fact that it is given only to a limited extent by bromides and not at all by chlorides.

The most remarkable reaction of this type given by potassium iodide is its reaction with anhydro α-hydroxymercuri-β-methoxy hydrocinnamic acid,  $C_6H_5-\underset{\textstyle OCH_3}{CH}-\!\!-\underset{\textstyle Hg-O}{CH-C}=O$, forming α mercury di-β-phenyl-anhydro-hydracrylic acid,— 

$$\begin{array}{l} C_6H_5-CH-CH-CO_2H \\ \qquad\quad\; | \qquad\;\; | \\ \qquad\quad\; O \qquad Hg \\ \qquad\quad\; | \qquad\;\; | \\ C_6H_5-CH-CH-CO_2H \end{array}$$

.[98]

This interesting substance has only been tested for its action with sulfides and acids towards both of which it is unusually stable.

The hypothesis that the change from R — Hg — X to R_2Hg requires some reagent which is capable of removing mercuric ions either as metallic mercury or as some slightly ionized complex [99] leads to ex-

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[97] Whitmore, *J. Am. Chem. Soc.* 41 (1919), 1850.

[98] Schoeller, Schrauth, and Struensee, *Ber.* 44 (1911), 1056.

[99] Whitmore, loc. cit.

periments on the action of potassium sulfocyanate on compounds of the type R — Hg — X. The stability of the sulfocyanate complexes of mercury would favor the formation of the R_2Hg compound according to the following equation,

$$2RHgX \longrightarrow R_2Hg + HgX_2,$$

the mercuric salt being removed by the sulfocyanate ions. Such appears to be the case when certain mercurated phenols and aromatic amines are refluxed with potassium sulfocyanate in aqueous alcohol. The corresponding substituted mercuribis-phenols and mercuribis-anilines are obtained.[100]

The sodium thiosulfate method is probably the most general for changing compounds of the type RHgX to those of the type R_2Hg in which both bonds of mercury are attached to carbon. It works best with substances which dissolve readily in the concentrated solution. On standing the R_2Hg compound separates leaving the inorganic mercury in the solution. In some cases the thiosulfate treatment gives an intermediate compound which can be isolated. This has the formula $R — Hg — S — SO_3Na$. The reaction has been carried out with the following substances:

(a) Phenyl mercuric compounds.[101]

(b) Substituted aniline and toluidine mercury compounds.[102]

(c) Mercury compounds of diphenyl amine and methyl diphenyl amine.[103] Tetra chloromercuri diphenyl amine gives a compound which has the two benzene nuclei attached by two mercury bridges.[104]

(d) Phenol mercury compounds.[105]

(e) Aminobenzoic acid mercury compounds.[106]

(f) Salicylic ester mercury compounds.[107]

The sulfide method for making R_2Hg has already been discussed under the reactions with sulfides. The organomercuric sulfide is usually prepared and dried and then heated at about 100°. The residue consisting of mercuric sulfide and the desired product is extracted with

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[100] Whitmore, unpublished results.

[101] Pesci, *Gazz. chim. ital.* 29 I (1899), 394. *Chem. Zentr.* 1899 II 481.

[102] Pesci, *Z. anorg. Chem.* 15 (1897), 212; 17 (1898), 282. Prussia, *Gazz. chim. ital.* 27 I (1897), 17. Dimroth, *Ber.* 35 (1902), 2041.

[103] Prussia, *Gazz. chim. ital.* 28 II (1898), 129. *Chem. Zentr.* 1898 II 928.

[104] Kharasch and Piccard, *J. Am. Chem. Soc.* 42 (1920), 1861.

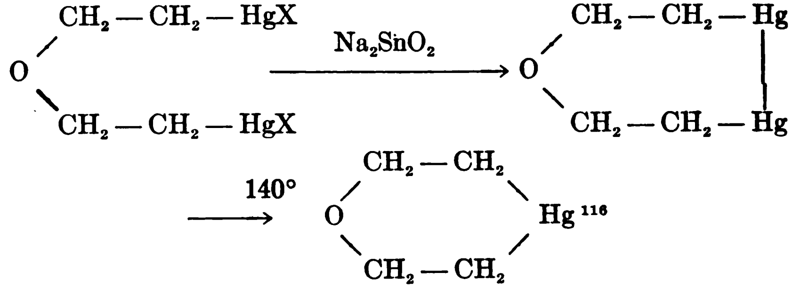
[105] Dimroth, *Chem. Zentr.* 1901 I 451. *Ber.* 35 (1902), 2855. Whitmore and Middleton, *J. Am. Chem. Soc.* 43 (1921), 622.

[106] Schoeller and Hueter, *Ber.* 47 (1914), 1936. Schoeller and Schrauth, *Ber.* 53 (1920), 642.

[107] *Ibid.*

benzene or carbon disulfide in which the former is insoluble. In the case of 2-acetoxymercuri-4-nitrophenol the action of sodium sulfide in the cold gives two kinds of complex sulfides. The first one formed has the usual formula $(RHg)_2S$. When heated it gives R_2Hg and a more complex sulfide $(RHg — S)_2Hg$ which can be recrystallized from acetone. On heating it gives 2HgS and R_2Hg.[108] The sulfide reaction has been applied in making mercury dimethyl,[109] mercury diphenyl,[110] various mercury dianilines,[111] mercury bis-acetanilide,[111] mercury disalicylic ester,[112] mercury dibenzoic ester,[113] mercury diphenols,[114] and 5-mercury-bis-3-nitro-4-hydroxyphenyl arsonic acid.[115]

The change to the R_2Hg compound can be brought about by reduction in neutral or alkaline media. Acid reduction is excluded as it removes the mercury completely. The commonest reducing agent used is an alkaline solution of sodium stannite. It seems probable that the process here takes the course which it does with inorganic mercury compounds forming a mercurous compound and then metallic mercury. In this case an organic "mercurous" compound of the type R — Hg — Hg — R is perhaps first formed. It then decomposes to metallic mercury and R — Hg — R. The only case in which the mercurous compound has been isolated is in the action of sodium stannite on the ethyl ether compounds obtained from ethylene.



If it is eventually proved that these ethyl ether compounds are really only molecular compounds the "mercurous" compound will have

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[108] Fourneau and Vila, *J. pharm. chim.* (7) 6 (1912), 433.

[109] Hilpert and Ditmar, *Ber.* 46 (1913), 3740.

[110] Dreher and Otto, *Ann.* 154 (1870), 116.

[111] Pesci, *Gazz. chim. ital.* 23 II (1893), 526. Piccinini, *Ibid.* 541. Ruspaggiari, *Ibid.* 547. *Chem. Zentr.* 1894 I 501. Pesci, *Z. anorg. Chem.* 15 (1897), 217.

[112] Schoeller and Schrauth, loc. cit. 640.

[113] *Ibid.* 637. Pesci, *Gazz. chim. ital.* 32 II (1902), 295. *Chem. Zentr.* 1902 II 1454.

[114] Dimroth, *Chem. Zentr.* 1901 I 451. Fourneau and Vila, loc. cit.

[115] Stieglitz, Kharasch, and Hanke, *J. Am. Chem. Soc.* 43 (1921), May ?

[116] Sand, *Ber.* 34 (1901), 2913.

to be regarded as an addition product of ethylene and mercurous oxide and the final product as one of ethylene and mercuric oxide.

In a few other cases a temporary purple or red color followed by the gray of metallic mercury may indicate the formation of a very unstable mercurous compound. Ordinarily there is no evidence of such an intermediate compound and the process may be represented by the equation,

$$2RHgX + 2NaOH + Na_2SnO_2 \rightarrow R_2Hg + Na_2SnO_3 + Hg + 2NaX + H_2O.$$

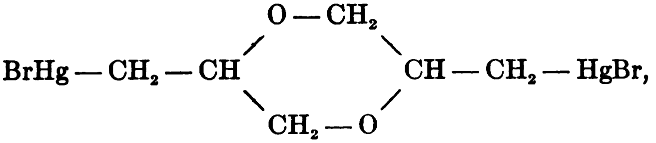
The process apparently differs from the corresponding inorganic reaction in that all of the mercury does not appear as metal even when an excess of sodium stannite is used.[116a] The sodium stannite reaction has been applied successfully in the following cases:—

(a) Ethyl mercuric chloride.[117]

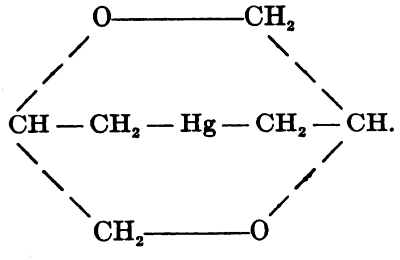
(b) Ethanol mercuric bromide,[118] $Br—Hg—CH_2—CH_2—OH$, gives metallic mercury and a volatile toxic substance of carbylamine odor. This is probably $Hg(CH_2—CH_2—OH)_2$, although it has not been analyzed.

(c) The action with the ethyl ether di-mercuric bromide has already been mentioned.

(d) Diepi-iodhydrine-dimercuric bromide,



obtained from allyl alcohol and mercuric salts reacts with sodium stannite giving a red precipitate which may be a mercurous compound. This immediately turns gray from the separation of mercury leaving the compound



[116a] Stieglitz, Kharasch, and Hanke, l. c.

[117] Dimroth, *Chem. Zentr.* 1901 I 451.

[118] Sand, *Ber.* 34 (1901), 1394.

(e) Phenyl mercuric chloride gives a black precipitate with sodium stannite. No odor of mercury diphenyl is noticed until this precipitate turns gray from the separation of mercury.[119]

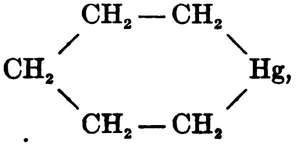
(f) o-Anisole mercuric iodide[120] gives the corresponding mercury dianisyl.

(g) Mercurated nitro- and dinitro-benzoic acids.[121]

(h) Cineol mercuric chloride gives mercury dicineolyl.[122]

(i) The reaction has also been applied to a number of hydroxy-carboxylic, hydroxy arsonic, and hydroxy sulfonic acids of benzene, toluene and naphthalene.[123]

Sodium amalgam in alcohol or even in dry benzene changes some organomercuric salts to the R_2Hg compounds. Pentamethylene dimercuric bromide gives cyclomercuripentamethylene,



and its polymers.[124] Phenyl mercuric iodide and acetate give mercury diphenyl.[125] α-Naphthyl mercuric iodide gives mercury dinaphthyl.[126]

Sodium metal can be used in place of sodium amalgam in some cases. The thiophene mercuric chlorides are changed to mercury dithienyls by heating in xylene with sodium. This is the only method for making the β-mercury dithienyls.[127]

Recent patents involve the use of such alkaline reducing agents as ferrous hydroxide or sodium hydrosulfite in the presence of sodium hydroxide. These reagents appear to be better for preparing the R_2Hg compounds in the cases of mercurated aromatic acids and phenols.

A number of special methods for making the mercury compounds of the type R_2Hg have been used in individual cases. Thus methyl mercuric iodide when distilled with potassium hydroxide or calcium

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[119] Dimroth, loc. cit. 449. Dimroth, *Ber.* 35 (1902), 2853.

[120] *Ibid.*

[121] *D. R. P.* 249,725, and 251,332. *Chem. Zentr.* 1912 II 1418. Fränkel, 670.

[122] Sand and Singer, *Ber.* 35 (1902), 3176.

[123] *D. R. P.* 255,030. *Chem. Zentr.* 1913 I 353.

[124] Hilpert and Grüttner, *Ber.* 47 (1914), 186.

[125] Dreher and Otto, *Ann.* 154 (1870), 115.

[126] Hilpert and Grüttner, loc. cit. 188.

[127] Steinkopf and Bauermeister, *Ann.* 403 (1914), 57. Steinkopf, *Ann.* 413 (1917), 328.

hydroxide gives a small yield of mercury dimethyl.[128] Phenyl mercuric chloride heated with dry silver oxide gives mercury diphenyl.[129] Phenyl mercuric iodide heated in alcohol with copper bronze gives mercury diphenyl in good yield.[130]

Phenyl mercuric acetate reacts with ammonium hydroxide giving a substance $(C_6H_5Hg)_2NH_2OAc$. This reacts with various sulfur compounds such as carbon disulfide and aromatic thioureas giving mercury diphenyl, mercuric sulfide and other products.[131]

V. The Reaction Between Organic Mercury Compounds of the Type R_2Hg and Mercuric Salts.

$$R_2Hg + HgX_2 \rightarrow 2RHgX.$$

This reaction takes place readily with all kinds of mercury compounds even in the case of the mercury α-dithienyls and mercuric iodide in which case the reaction goes so easily in the opposite direction. The reaction sometimes takes place in the cold but in general the substances have to be heated in alcohol or acetone solution. The reaction has only been carried out with salts of monobasic acids such as the mercuric halides, cyanide, sulfocyanate and organic salts like the acetate. It has been carried out with the following organomercuric compounds:—

(a) Mercury dimethyl.[132]

(b) Mercury diethyl.[133] Frankland's method of making ethyl mercuric chloride from zinc ethyl and an excess of mercuric chloride really involves this reaction as a smaller amount of mercuric chloride gives mercury diethyl.

(c) Alcoholic solutions of mercury diethyl [134] and mercuric chloride give an immediate precipitate of ethyl mercuric chloride.

(d) Mercury di-isoamyl.[135]

(e) Mercury di-cyclohexyl.[136]

(f) Cyclomercuripentamethylene [137] and its polymers in benzene

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[128] Buckton, *Ann.* 108 (1858), 104.

[129] Otto, *J. prakt. Chem.* (2) 1 (1870), 184.

[130] Whitmore, unpublished results.

[131] Pesci, *Gazz. chim. ital.* 39 I (1909), 150.

[132] Buckton, loc. cit. 105.

[133] Frankland, *Ann.* 111 (1859), 60.

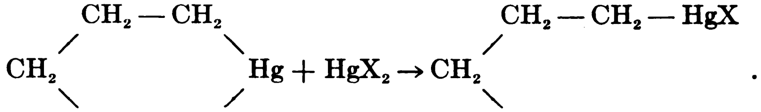
[134] Frankland and Duppa, *J. Chem. Soc.* 16 (1863), 415.

[135] Frankland and Duppa, loc. cit. 422. *Ann.* 130 (1864), 114.

[136] Grüttner, *Ber.* 47 (1914), 1655.

[137] Hilpert and Grüttner, *Ber.* 47 (1914), 191.

solution readily act with ether solutions of the mercuric halides giving precipitates of the corresponding pentamethylene di-mercuric halides.



(g) Mercury diphenyl[138] reacts easily with mercuric salts in alcohol or acetone. Thus a mixture of mercury diphenyl and the calculated amount of mercuric iodide refluxed with a little alcohol until the color of the iodide disappears gives a quantitative yield of pure phenyl mercuric iodide. Mercury diphenyl heated with mercurous chloride at 160° gives phenyl mercuric chloride and metallic mercury. The reaction between mercury diphenyl and mercuric thiocyanate requires a temperature of 120°.

(h) The homologs of mercury diphenyl give the reaction. In some cases the mixtures have to be heated with alcohol in sealed tubes to complete the process.[139]

(i) Mercury dibenzyl.[140]

(j) Mercury di-anilines.[141]

(k) Mercury di-anisoles and di-pthenetoles.[142]

(l) α-Mercury dinaphthyl[143] does not react with mercuric chloride when heated in carbon disulfide. The original substances are recovered. The reaction however takes place easily in alcohol and acetone. Thus 1 gm. of the mercury dinaphthyl is suspended in 50 c.c. of hot acetone and treated with .6 gm. of mercuric chloride. All goes into solution. The addition of water precipitates the naphthyl mercuric chloride.

(m) β-Mercury dinaphthyl[144] reacts with mercuric halides in hot amyl alcohol.

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[138] Otto, loc. cit. 180. Dreher and Otto, *Ann.* 154 (1870), 113. Steinkopf, *Ann.* 413 (1917), 313.

[139] Otto, loc. cit. 185. Michaelis, *Ber.* 28 (1895), 589.

[140] Wolff, *Ber.* 46 (1913), 65. Jones and Werner, *J. Am. Chem. Soc.* 40 (1918), 1268.

[141] Michaelis and Rabinerson, *Ber.* 23 (1890), 2342. Pesci, *Gazz. chim. ital.* 23 II (1893), 532. *Chem. Zentr.* 1894 I 501. *Gazz. chim. ital.* 28 II (1898), 106. *Chem. Zentr.* 1898 II 546. *Z. anorg. Chem.* 17 (1898), 280. Whitmore, *J. Am. Chem. Soc.* 41 (1919), 1853.

[142] Michaelis and Rabinerson, loc. cit. 2345. Dimroth, *Ber.* 32 (1899), 764. Michaelis, *Ber.* 27 (1895), 257.

[143] Otto and Möries, *Ann.* 147 (1868), 179. Otto, *Ann.* 154 (1870), 190. Otto, *J. prakt. Chem.* (2) 1 (1870), 185. Steinkopf, *Ann.* 413 (1917), 313, 330.

[144] Michaelis, loc. cit. 251.

(n) All mercury dithienyl compounds[145] react with mercuric halides in acetone giving the corresponding thiophene mercuric halides which can be precipitated by the addition of water.

VI. The Reaction with Halogens.

As has already been stated, the compounds R_2Hg react with halogens giving an organic halide and $R-Hg-X$ which can react with more halogen giving more of the organic halide and a mercuric halide, according to the equations,

$$R_2Hg + X_2 = R-X + RHgX$$
$$RHgX + X_2 = R-X + HgX_2.$$

The reaction has been carried out with the following compounds:

(a) Mercury dimethyl.[146]

(b) Methyl mercuric acetate.[147]

(c) Mercury diethyl catches fire in chlorine gas. It reacts less violently with bromine and iodine.[148]

(d) Ethyl mercuric hydroxide reacts with bromine forming ethyl mercuric bromide.[149]

(e) Mercury di-n-propyl.[150]

(f) Mercury di-isobutyl.[151]

(g) Mercury di-*sec*-butyl, formed by the reduction of methyl ethyl ketone with a mercury cathode, reacts with iodine in ether solution giving the corresponding butyl mercuric iodide and butyl iodide.[152]

(h) Mercury di-isoamyl.[153]

(i) Mercury dioctyl.[154]

(j) Allyl mercuric iodide reacts quantitatively with iodine giving allyl iodide. This reaction is used in separating allyl iodide from isopropyl iodide. The former gives a crystalline compound when treated with mercury while the latter does not. The purified mercury compound is then treated with iodine to make pure allyl iodide.[155]

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[145] Steinkopf, loc. cit. 813.

[146] Buckton, *Ann.* 108 (1858), 104. Frankland and Duppa, *J. Chem. Soc.* 16 (1863), 417. Hilpert and Ditmar, *Ber.* 46 (1913), 3740.

[147] Otto, *Ann.* 154 (1870), 199.

[148] Buckton, *Ann.* 112 (1859), 221. *J. prakt. Chem.* (1) 79 (1860) 107. Chapman, *J. Chem. Soc.* 19 (1866), 150.

[149] Dünhaupt, *J. prakt. Chem.* (1) 61 (1854), 425. *Ann.* 92 (1854), 379.

[150] Cahours, *Compt. rend.* 76 (1873), 135, 749. *Ber.* 6 (1873), 567.

[151] Cahours, *J. prakt. Chem.* (2) 8 (1873), 398. *Compt. rend.* 77 (1873), 1405.

[152] Tafel, *Ber.* 39 (1906), 3631.

[153] Frankland and Duppa. *J. Chem. Soc.* 16 (1863), 421. *Ann.* 130 (1864), 112.

[154] Eichler, *Ber.* 12 (1879), 1881.

[155] Linnemann, *Ann. Spl.* 3 (1865), 262.

(k) Iodomethylmercuric iodide reacts with iodine giving methylene iodide.[156]

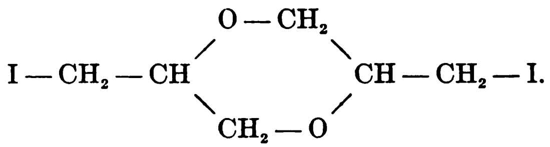
(l) Chloromethyl mercuric iodide prepared from the above iodo compound by mercuric chloride reacts with iodine giving methylene chloroiodide.[157]

(m) β-Acetoxymercuriethyl methyl ether obtained from the action of ethylene on mercuric acetate in methyl alcohol solution decolorizes an ether solution of iodine instantly. The products have not been studied.[158]

(n) Ethanolmercuric iodide obtained from ethylene and an aqueous solution of a mercuric salt reacts with iodine dissolved in potassium iodide giving a 60% yield of ethylene iodohydrine.[159] The formation of the iodohydrine could also be explained by the "molecular formula" for the mercurated ethylene, $C_2H_4.Hg(OH)I$. The basic mercuric iodide would act with iodine forming hypoiodous acid which would then add to the ethylene.

(o) Diethylether di-mercuric iodide, also obtained from ethylene, reacts with iodine in potassium iodide solution giving a 90% yield of ββ′-di-iodo diethyl-ether.[160]

(p) Di-epi-iodohydrine di-mercuric iodide obtained from allyl alcohol reacts with iodine giving di-epi-iodohydrine,[161]



In this case the reaction is carried out in benzene in a sealed tube at 140°.

(q) Trichloromercuri-acetaldehyde(?), obtained from acetylene and mercuric chloride, reacts with chlorine water giving mercuric chloride and chloral which is identified by changing it to chloroform. Iodine gives an entirely different reaction but the organic product has not been identified.[162]

(r) The products obtained from acetylene and mercuric chromate,

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[156] Sakurai, *J. Chem. Soc.* 37 (1880), 660.
[157] Sakurai, *J. Chem. Soc.* 41 (1882), 360.
[158] Schoeller and Schrauth, *Ber.* 46 (1913), 2867.
[159] Sand, *Ber.* 34 (1901), 1388.
[160] *Ibid.* 1391. Sand, *Ber.* 34 (1901), 2908.
[161] Sand, loc. cit. 1393.
[162] Biltz and Mumm, *Ber.* 37 (1904), 4423.

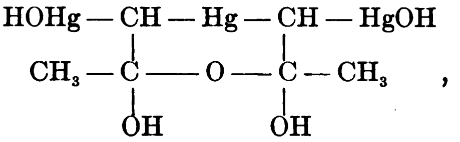
chlorate, and fluorsilicate react with iodine giving iodoform readily.[163] Mercury acetylide acts with iodine giving diiodoacetylene.[164] When mercury acetylide is treated with mercuric chloride it gives the same white precipitate which is obtained from acetylene and mercuric chloride (trichloromercuri-acetaldehyde ?). This gives no diiodoacetylene with iodine.[165]

The product from phenyl acetylene and mercuric salts reacts with bromine giving a product which may be dibromoacetophenone but which has not been actually identified.[166]

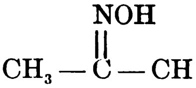
(s) Mercury bis-monochloroacetylene reacts with an ethereal solution of iodine giving chlorotriiodoethylene.[167]

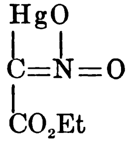
(t) Mercury bis-trichloroethylene reacts with chlorine only in strong sunlight. It gives mercuric chloride and perchloroethane.[168]

(u) The product from acetone and mercuric oxide,



$$\begin{array}{ccccccccc} HOHg & — & CH & — & Hg & — & CH & — & HgOH \\ & & | & & & & | & & \\ CH_3 & — & C & — & O & — & C & — & CH_3 \\ & & | & & & & | & & \\ & & OH & & & & OH & & \end{array} ,$$

reacts with bromine in potassium bromide solution giving an oil having a sharp odor. When this is steam distilled and treated with hydroxylamine it gives monomethyl glyoxime,  $CH_3 — \overset{\overset{\displaystyle NOH}{\|}}{C} — CH = NOH$, indicating that the brominated oil is unsymmetrical dibromoacetone.[169]

(v) Anhydro hydroxymercuri nitroacetic ester,  $\begin{array}{l} HgO \\ |\ \ \ | \\ C = N = O \\ | \\ CO_2Et \end{array}$, reacts with bromine giving dibromo nitro acetic ester.[170]

(w) Mercury diazoacetic ester reacts with iodine giving yellow

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[163] Nieuwland and Maguire, *J. Am. Chem. Soc.* 28 (1906), 1026.

[164] Keiser, *Am. Chem. J.* 15 (1893), 537.

[165] Plimpton and Travers, *J. Chem. Soc.* 65 (1894), 267.

[166] Manchot and Haas, *Ann.* 399 (1913), 143. Biltz and Reinkober, *Ann.* 404 (1914), 233.

[167] Hofmann and Kirmreuther, *Ber.* 42 (1909), 4235.

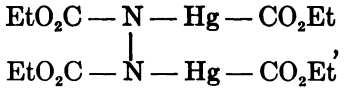
[168] *Ibid.* 4232.

[169] Auld and Hantzsch, *Ber.* 38 (1905), 2683.

[170] Scholl and Nyberg, *Ber.* 39 (1906), 1957.

mercuric iodide. No gas is evolved. The organic product is explosive.[171]

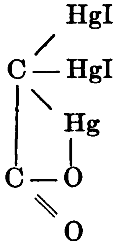
(x) Chloromercuriformic methyl ester reacts with iodine in ether giving a solution which apparently contains iodoformic ester as treatment with ammonia gives a 68% yield of methyl urethane.[172] The ethyl compound gives a similar result. A compound having a C — Hg grouping identical with that in this ester is the compound,



$$\begin{array}{c} EtO_2C - N - Hg - CO_2Et \\ | \\ EtO_2C - N - Hg - CO_2Et \end{array},$$

obtained from mercuric oxide and hydrazine monocarboxylic ethyl ester, $NH_2 - NH - CO_2Et$. Treatment with bromine in benzene gives bromoformic ester which is recognized by its lachrymatory properties and by its conversion into ethyl urethane. The other organic product of the bromination is azodicarboxylic ester.[173]

(y) The di-iodide of anhydro tri-hydroxymercuri acetic acid,



, reacts with iodine giving iodoform.[174]

(z) β-Mercuribis-propionic ester decolorizes a warm alcoholic solution of iodine at once. The organic products have not been identified.[175] The corresponding mercurated acid reacts with iodine in potassium iodide giving a dark crystalline precipitate which acts like a periodide.

(a′) Pentamethylene di-mercuric iodide reacts with iodine in benzene only on long boiling. It forms pentamethylene di-iodide.[176] Cyclomercuripentamethylene reacts with bromine and iodine giving pentamethylene di-mercuric bromide and iodide.[177] This result is at variance with the usual course of the reaction of R_2Hg compounds with halogens. If the cyclomercuripentamethylene is really a six membered

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[171] Buchner, *Ber.* 28 (1895), 219.

[172] Schoeller and Schrauth, *Ber.* 46 (1913), 2874.

[173] Diels and Uthemann, *Ber.* 53 (1920), 729.

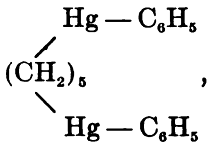
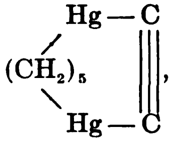
[174] Sand and Singer, *Ber.* 36 (1903), 3709.

[175] E. Fischer, *Ber.* 40 (1907), 388.

[176] Hilpert and Grüttner, *Ber.* 47 (1914), 182.

[177] *Ibid.* 190.

ring containing mercury the product would be expected to have only one mercury in the molecule. There is no explanation of the failure of this reaction to take place in the usual way. There seems to be no doubt that the dimercurated compounds are obtained as they have been identified by analysis and by mixed melting point determinations with the known bromide and iodide. Both of the polymers give the same results with iodine as the simple substance.

(b′) Pentamethylene di-mercuriphenyl,  , reacts with a benzene solution of iodine at 35° giving pentamethylene di-mercuric iodide.[178] Pentamethylene di-mercuriacetylide , reacts quickly with iodine in hot benzene forming mercuric iodide, pentamethylene di-iodide and di-iodoacetylene.[178]

(c′) Phenyl mercuric compounds react readily with halogens in the usual way.[179]

(d′) The tolyl mercuric chlorides react with bromine giving o- and p-tolyl bromides.[180]

(e′) Mercurated nitrobenzenes react with bromine forming the corresponding bromonitrobenzenes.[181]

(f′) The monomercurated phenols give ortho and para iodophenols with an ether solution of iodine. Mercurated p-cresol gives similar results.[182]

(g′) The mercurated nitrophenols react with bromine and iodine giving the corresponding bromo- and iodonitrophenols.[183]

(h′) Mercurated benzoic acid reacts with bromine in potassium bromide solution giving the potassium salt of o-bromobenzoic acid thus

[178] Hilpert and Grüttner, *Ber.* 47 (1914), 184.

[179] Otto, *J. prakt. Chem.* (2) 1 (1870), 182. Dreher and Otto, *Ann.* 154 (1870), 108. Söderbäck, *Ann.* 419 (1919), 273.

[180] Dreher and Otto, *Ann.* 154 (1870), 173. Dimroth, *Ber.* 32 (1899), 761.

[181] Dimroth, *Ber.* 35 (1902), 2037. Kharasch and Chalkley, *J. Am. Chem. Soc.* 43 (1921), 611.

[182] Dimroth, *Ber.* 31 (1898), 2155; 35 (1902), 2359. Brieger, *Arch. Pharm.* 250 (1912), 62. *Chem. Zentr.* 1912 I 753.

[183] Hantzsch and Auld, *Ber.* 39 (1906), 1114.

proving that the mercury enters the ortho instead of the meta position.[184]

(i′) Mercurated salicylic acid is proved to have the mercury in the position ortho to the hydroxyl group by treating it with iodine and then fusing the iodosalicylic acid obtained with potassium hydroxide. The product is pyrocatechol-o-carboxylic acid.[185]

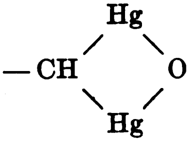
(j′) In determining the position of mercuri groups in anilines it is advisable to change the anilines to the corresponding acetanilides before treatment with iodine or bromine.[186] If this is not done more halogens may enter the nucleus than the number corresponding to the mercuri groups originally present. Thus "phenylated white precipitate" gives a mixture of mono- and diiodoanilines although it contains but one mercury in the molecule.[187]

(k′) Acetoxymercuriphenylglycine ethyl ester reacts with bromine and iodine giving compounds which probably have the halogen in the ortho position.[188]

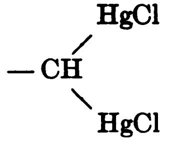
(l′) The mercurated quarternary ammonium compounds obtained from the mercurated anilines and alkyl halides react with an excess of bromine giving the corresponding mercury-free bromides.[189] Thus $[Cl(CH_3)_3N-C_6H_4-]_2Hg$ reacts with bromine giving $Cl(CH_3)_3N-C_6H_4-Br$.

(m′) Phenacylmercuric chloride gives bromoacetophenone.[190]

(n′) The mercurated nitrotoluenes containing the groups



and



react with halogens giving the corresponding benzal halides.[191] When these are boiled with sodium carbonate they are converted into the corresponding nitrobenzaldehydes.

(o′) Mercurated anthranilic acid has the mercury in the para po-

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[184] Dimroth, *Ber.* 35 (1902), 2871.

[185] *Ibid.* 2873.

[186] Dimroth, *Ber.* 35 (1902), 2040. Vecchiotti, *Gazz. chim. ital.* 44 II (1914), 37. Schoeller, Schrauth, and Rother, *Ber.* 45 (1912), 2817. J. Rother, *Dissert.*, Berlin, 1911, p. 45 and 58.

[187] Rudolph, *Ber.* 11 (1878), 78. J. Rother, loc. cit. 16.

[188] Schoeller, Schrauth, and Goldacker, *Ber.* 44 (1911), 1302.

[189] Pesci, *Gazz. chim. ital.* 23 II (1893), 526. *Z. anorg. Chem.* 15 (1897), 208.

[190] Dimroth, *Ber.* 35 (1902), 2870.

[191] Reissert, *Ber.* 40 (1907), 4213.

sition to the amino group as is proved by converting it to the iodo compound.[192] This difference from the result of mercurating salicylic acid is interesting.

(p′) α-Mercury dinaphthyl reacts with iodine and bromine in the usual way. The first iodonaphthalene was prepared in this way.[193]

(q′) Mercurated-β-naphthol carboxylic acid is changed to the iodo compound easily.[194]

(r′) α-Thiophene mercuric chloride does not act with iodine.

(s′) The corresponding αα′ dimercurated thiophene readily forms di-iodothiophene. When the dimercurated compound is refluxed with bromine water it gives a mixture of di-, tri- and tetra brominated thiophenes.[195] α′-iodo-α-thiophene mercuric chloride gives di-iodothiophene.[196]

(t′) Mercurated camphor reacts with iodine in benzene giving di-iodo-camphor which can be changed to camphor quinone.[197] The same product is obtained with iodine chloride or iodine bromide.[198]

(u′) Cineol mercuric iodide on treatment with an ether solution of iodine in the cold gives a liquid iodide which may be cineol iodide.[199]

VII. Reaction with Halides and Cyanides of Metals.

The reaction of iodides in forming compounds of the form R_2Hg has already been discussed under IV. The other reactions of metallic halides may be divided into two classes, those which result in a simple metathesis and those which result in the splitting of the C — Hg linkage. The substances which have their C — Hg linkages broken are of two types, mercuration products obtained by simple substitution, and mercuration products obtained by the addition of the groups — HgX and — OH to an unsaturated acid.

$$\mathrm{RHgX + KI + H_2O \rightarrow R-H + HgI_2} + KOH$$
$$\mathrm{R-CHOH-CH(HgI)-CO_2K + KI \rightarrow}$$
$$\mathrm{R-CH=CH-CO_2K + HgI_2} + KOH$$

In either case one molecule of base is formed for each C — Hg linkage broken.

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[192] Schoeller and Hueter, *Ber.* 47 (1914), 1938.
[193] Otto, *Ann.* 154 (1870), 189.
[194] Brieger and Schulemann, *J. prakt. Chem.* (2) 89 (1914), 176.
[195] Volhard, *Ann.* 267 (1892), 180.
[196] Steinkopf and Bauermeister, *Ann.* 403 (1914), 62, 69.
[197] Marsh and Fleming-Struthers, *J. Chem. Soc.* 95 (1909), 1786.
[198] Marsh, *J. Chem. Soc.* 97 (1910), 2413.
[199] Sand and Singer, *Ber.* 35 (1902), 3177.

The simple metathetical reaction is very useful in preparing the organomercuric halides from the more soluble compounds such as the acetates, nitrates, and sulfates. In many cases in which mercuric acetate is the mercurating agent the resulting acetate is so soluble that it cannot be isolated. In these cases the original reaction mixture is treated with sodium chloride solution which precipitates the corresponding chloride. This method has received the widest application to cases varying from the mercuration products of ethylene to those of the most complicated naphthalene dye intermediates. Whenever the alkali halides are to be used for these precipitation reactions the other two possible results must be kept in mind. For instance thiophene mercuric chloride treated with sodium iodide would be expected to give the iodide. In reality, considerable of the R_2Hg compound, mercury dithienyl, is obtained. The reaction may fail in a different way when applied to a substance like diacetoxymercurimalonic ester. Instead of the expected di-iodide the product is malonic ester, the C — Hg linkages being split entirely.

The splitting of the C — Hg linkage by alkali halides takes place most readily with the inorganic iodides. The bromides act very little in this way and the chlorides almost not at all. Only a few types of organic mercury compounds undergo this splitting. Among these are mercury derivatives of malonic ester and malonic acid, and cyanoacetic acid.[200] In sharp contrast to the behaviour of these compounds is the fact that mercurated nitroacetic ester is unchanged by potassium iodide.[201] The mercuration products of many unsaturated acids are changed to the original unsaturated acids by the action of potassium iodide. The acids which have been studied in this way are acrylic acid, crotonic acid, maleic acid, citraconic acid, and itaconic acid.[202] The mercurated anhydro compounds of these acids show an interesting difference in their action with chlorides and iodides. Although the anhydrides are insoluble in water they readily dissolve in solutions of chlorides or iodides giving neutral and strongly alkaline solutions respectively. The difference may be illustrated by the acrylic acid compound

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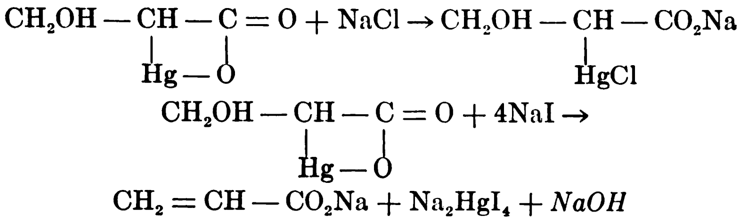
[200] Billmann, *Ber.* 35 (1902), 2581. Billmann and Witt, *Ber.* 42 (1909), 1070. Petterson, *J. prakt. Chem.* (2) 86 (1912), 464.

[201] Scholl and Nyberg, *Ber.* 39 (1906), 1957.

[202] Billmann, loc. cit. 2571. *Ber.* 43 (1910), 574.



$$CH_2OH-\underset{\underset{\displaystyle Hg-O}{|\qquad|}}{CH-C}=O+NaCl\rightarrow CH_2OH-\underset{\underset{\displaystyle HgCl}{|}}{CH}-CO_2Na$$

$$CH_2OH-\underset{\underset{\displaystyle Hg-O}{|\qquad|}}{CH-C}=O+4NaI\rightarrow$$

$$CH_2=CH-CO_2Na+Na_2HgI_4+\mathit{NaOH}$$

In the second case a titration with standard acid shows the presence of .86 equivalent of base indicating that the splitting of the C — Hg linkage is almost quantitative. This reaction is shown only by the addition products of unsaturated *acids*. The unsaturated hydrocarbons and alcohols give addition products which react with inorganic iodides giving complex iodides of great stability. In the case of the products from ethylene the iodides can even be recrystallized from hot alkalies without decomposition.

The mercurated phenols are decomposed by boiling with potassium iodide solution. Titration shows almost exactly one equivalent of alkali formed for each C — Hg linkage.[203] Potassium bromide gives the same splitting to a limited extent while potassium chloride does not give it at all. When the phenolic hydroxyl is no longer present as in the corresponding acetylated phenols, iodides no longer cause any splitting of the C — Hg. This allows play to the other important iodide reaction, namely, the formation of the R_2Hg compounds. Thus the acetylated phenol mercuric chlorides react with an excess of potassium iodide giving the corresponding acetylated mercury diphenols. These different reactions may be illustrated by the equations:

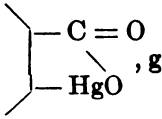
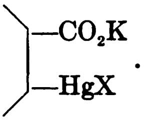
$$HO-C_6H_4-HgCl+4KI+H_2O\rightarrow C_6H_5OH+KCl+K_2HgI_4+\mathit{KOH}$$
$$2AcO-C_6H_4-HgCl+4KI\rightarrow(AcO-C_6H_4-)_2Hg+2KCl+K_2HgI_4.$$

In sharp contrast to the action of the mercurated phenols the mercurated nitrophenols give no action with potassium iodide.[204]

Mercurated benzoic acid is split by sodium halides with the formation of sodium hydroxide. The iodide has the greatest effect and the chloride the least.[205]

Anhydro p-hydroxymercuri-anthranilic acid is said to be soluble in potassium iodide but less soluble in potassium bromide and still less in potassium chloride. This is hard to understand if the solubility

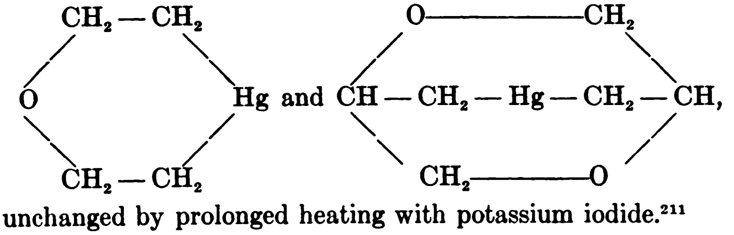
[203] Whitmore and Middleton, *J. Am. Chem. Soc.* 43 (1921), 622.
[204] Hantzsch and Auld, *Ber.* 39 (1906), 1110.
[205] Pesci, *Gazz. chim. ital.* 32 II (1902), 277.

depends merely on a salt formation as it usually does,  , giving  .

It may be that the increased solubility in iodides indicates a splitting of the C — Hg and a corresponding formation of alkali.[206]

The mercuration products of the naphthol and naphthylamine intermediates of the dye industry are almost all split by alkali halides.[207] In many cases the extent of the splitting has been measured by titrations of the base formed. In others the "loosening" effect of the halide has been detected by means of ammonium sulfide. In many cases the mercurated compound gives no action with ammonium sulfide but if treated with a halide and then with the sulfide gives mercuric sulfide almost immediately. Both methods of study show that the splitting effect increases from chloride to *iodide.*

A number of miscellaneous observations of the action of halides may be mentioned. Iodomethyl mercuric iodide, $I—CH_2—HgI$, if heated with potassium iodide gives a brown insoluble substance and a sublimate of methyl mercuric iodide.[208] Methylene di-mercuric iodide gives the same reaction with potassium iodide.[209] Ethylene di-mercuric iodide, $IHg—CH_2—CH_2—HgI$, obtained from ethane hexamercarbide is partly soluble in an excess of potassium iodide solution. In sunlight this solution gives some mercuric iodide.[210] The reaction has not been further studied. The cyclic mercury compounds obtained indirectly from ethylene and allyl alcohol,



are unchanged by prolonged heating with potassium iodide.[211]

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[206] Schoeller and Hueter, *Ber.* 47 (1914), 1936.

[207] Brieger and Schulemann, *J. prakt. Chem.* (2) 89 (1914), 105.

[208] Sakurai, *J. Chem. Soc.* 39 (1881), 487.

[209] *Ibid.*

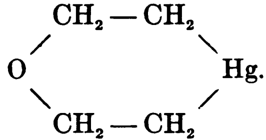
[210] Hofmann, *Ber.* 33 (1900), 1339.

[211] Sand, *Ber.* 34 (1901), 2914.

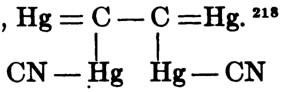
Ethane hexamercarbide reacts with cold solutions of alkali halides giving the salts $C_2Hg_6O_2X_2$ and bases. In this case, this does not indicate a splitting of the C — Hg linkage. The soluble base is formed by the action of the halides on the insoluble base forming still more insoluble salts.[212]

Stannous chloride reacts with mercury dimethyl forming a crystalline compound.[213] When this is treated with water it gives a soluble tin compound and a precipitate of methyl mercuric chloride.

Potassium cyanide has a splitting effect on the C — Hg linkage in many cases in which the iodides do not. Thus the ethanol-mercuric compounds and the ethyl ether mercuric compounds obtained from ethylene react with cyanide solutions giving ethylene as soon as warmed.[214]

In sharp contrast to the action of diethylether di-mercuric halides is the action of the cyclic mercury compound obtained from them by sodium stannite solution,  This substance is not changed by potassium cyanide solution even on prolonged boiling.[215] The mercury compounds obtained from allyl alcohol are not decomposed by potassium cyanide.[216]

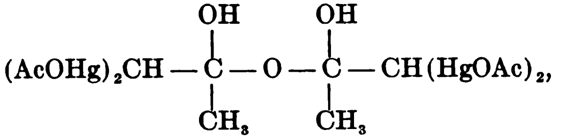
The mercury compounds obtained from di-cyclopentadiene by addition of the groups —HgCl and —OCH_3 or —OC_2H_5 react with boiling potassium cyanide solution forming di-cyclopentadiene.[217]

Ethane hexamercarbide on boiling with potassium cyanide loses one-third of its mercury forming the compound, 

$$\begin{array}{cc} Hg = \underset{\displaystyle CN-Hg}{\overset{}{\underset{|}{C}}} - \underset{\displaystyle Hg-CN}{\underset{|}{C}} = Hg. \end{array}$$

[218]

Tetra-acetoxymercuri-di-acetone hydrate



$$(AcOHg)_2CH - \underset{CH_3}{\overset{OH}{C}} - O - \underset{CH_3}{\overset{OH}{C}} - CH(HgOAc)_2,$$

reacts with potassium cyanide giving acetone.[219]

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[212] Hofmann, *Ber.* 33 (1900), 1335.

[213] Buckton, *Ann.* 108 (1858), 105.

[214] Hofmann and Sand, *Ber.* 33 (1900), 1344.

[215] Sand, *Ber.* 34. (1901), 2914.

[216] Hofmann and Sand, loc. cit. 1359 and 2700. Sand, loc. cit. 2915.

[217] Hofmann and Seiler, *Ber.* 39 (1906), 3188.

[218] Hofmann, *Ber.* 33 (1900), 1338.

[219] Sand and Genssler, *Ber.* 36 (1903), 3703.

The mercurated acetic acids and acetaldehydes react with warm potassium cyanide giving potassium acetate and acetaldehyde respectively.[220] Mercury bis-monochloroacetylene reacts rapidly with potassium cyanide giving monochloroacetylene.[221] Mercury bis-trichloroethylene acts only slowly with cyanide solutions. The bromine compounds act the same as the chlorides.

VIII. The Reaction with Halides of Non-Metals.

This reaction is almost the only one in which the organic compounds of mercury exactly parallel those of zinc and magnesium. Even in this case the mercury compounds are less reactive.

Boron trichloride reacts giving mercuric halides and compounds of the type $R - BCl_2$. It reacts with mercury diphenyl, mercury ditolyls, and mercury dinaphthyl only on heating to about 150°.[222] On the other hand it reacts in the cold with mercury di-anisoles and mercury diphenetoles.[223]

Phosphorus trichloride reacts with mercury dimethyl forming methyl mercuric chloride.[224] With mercury dipropyl it forms tripropyl phosphine.[225] Allyl mercuric iodide does not react with phosphorus tribromide even on heating.[226]

In general aromatic mercury compounds react with phosphorus trichloride at a high temperature giving the dichloro aromatic phospines, $R - PCl_2$. The reaction has been carried out with phenyl, o- and p-tolyl, xylyl, p-anisyl, and p-phenetyl mercury compounds.[227] Phosphenyl chloride, $C_6H_5PCl_2$ reacts with p-tolyl mercuric bromide giving p-tolyl phenyl chlorophosphine.[228]

Arsenic trichloride reacts with mercury dipropyl giving tripropyl arsine.[229] Mercury diphenyl and phenyl mercuric chloride react with arsenic trichloride giving phenyl dichloroarsine.[230] Mercury dithienyl

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[220] Hofmann, *Ber.* 31 (1898), 1908 and 2213; 32 (1899), 875; 37 (1904) 4460. Hofmann and Kirmreuther, *Ber.* 42 (1909), 4237.

[221] Hofmann and Kirmreuther, loc. cit. 4233. *Ber.* 41 (1908), 317.

[222] Michaelis and Becker, *Ber.* 13 (1880), 59 and 180. Michaelis, *Ber.* 27 (1894), 247.

[223] *Ibid.* 254.

[224] Buckton, *Ann.* 108 (1858), 105.

[225] Cahours, *Ber.* 6 (1873), 568.

[226] Oppenheim, *Ber.* 4 (1871), 671.

[227] Michaelis, *Ann.* 293 (1896), 196, 248, 257, 291, 303, 313.

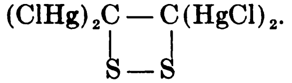
[228] Pope and Gibson, *J. Chem. Soc.* 101 (1912), 737.

[229] Cahours, loc. cit. 568.

[230] Michaelis, *Ann.* 201 (1880), 197 and 217. Roeder and Blasi, *Ber.* 47 (1914), 2748.

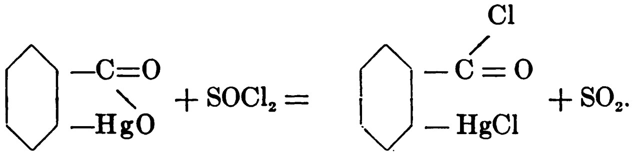
and thiophene mercuric halides react smoothly to form the thiophene arsenic compounds of the types $R-AsCl_2$ and R_2AsCl.[231]

The reaction of sulfur monochloride with organic mercury compounds has been studied only in the case of ethane hexamercarbide and its salts.[232] $C_2Hg_6Cl_6$ will not act even at 120°. The base, $C_2Hg_6O_4H_2$ reacts with a 10% solution of sulfur monochloride in benzene giving a yellow compound containing only four atoms of mercury,



$$\begin{array}{c} (\mathrm{ClHg})_2\mathrm{C}-\mathrm{C}(\mathrm{HgCl})_2. \\ |\qquad\ | \\ \mathrm{S}-\mathrm{S} \end{array}$$

Thionyl chloride reacts with mercury aromatic compounds giving the corresponding aromatic mercuric chloride.[236] Recently it has been found that thionyl chloride will react with anhydro hydroxymercuribenzoic acid giving the mercurated acid chloride.[237]



Thionyl chloride is said to react on α-mercury dinaphthyl with the formation of β-naphthyl chloride.[238]

IX. Reaction with Alkyl and Aryl Halides.

The heating of an alkyl mercuric iodide with an alkyl iodide might be expected to give mercuric iodide and a lengthened carbon chain. However, such is not the case. There are only two instances in which a reaction like this is known to take place and neither one of them involves an alkyl halide. When benzal chloride is heated with mercury diphenyl some triphenyl methane is obtained.[239] When allyl mercuric iodide is heated with allyl iodide the product is "probably" diallyl.[240] In view of the fact that allyl mercuric iodide when heated alone gives diallyl this action is not very significant.

[231] Finzi, *Gazz. chim. ital.* 45 II (1915), 283. *Chem. Zentr.* 1916 I 474. Steinkopf, *Ann.* 413 (1917), 317.

[232] Hofmann and Feigel, *Ber.* 38 (1905), 3655.

NOTE.—Reference numbers 233, 234 and 235 are omitted.

[236] Michaelis and Godchaux, *Ber.* 24 (1891), 758.

[237] Sachs, *Ber.* 53 (1920), 1740.

[238] Heumann and Köchlin, *Ber.* 16 (1883), 1626.

[239] Kekulé and Franchimont, *Ber.* 5 (1872), 907.

[240] Linnemann, *Ann. Spl.* 3 (1865), 262.

When mercury diethyl is heated with allyl iodide in a tube at 120° for two days the products are ethyl mercuric iodide, ethyl iodide, and diallyl.[241] These products could be explained by assuming that allyl iodide on heating tends to give iodine and diallyl. The iodine would act on the mercury diethyl giving the observed products. In a similar way mercury diethyl reacts with iodoform at 100° giving acetylene, ethylene, ethyl iodide and ethyl mercuric iodide. This complex reaction is all the more remarkable in that it starts even at 70°.[242] Mercury diethyl does not react with cold bromoacetic ethylester but when heated to 150° gives a gas which is "probably" ethylene. The other products are ethyl mercuric bromide and ethyl acetate.[243]

Methylene dimercuric iodide heated with ethyl iodide or bromide at 140° gives methyl mercuric iodide.[244]

Ethane hexamercarbide heated with ethyl iodide and ether for 60 hours at 90° gives $C_2Hg_6I_6$ and a small amount of mercuric iodide. The volatile products have not been studied.[245]

Mercury diphenyl heated with ethylene dibromide at 200° for 8 hours gives phenyl mercuric bromide. No other product has been identified.[246]

Mercury malonic ester gives no mercuric iodide even on long boiling with ethyl iodide.[247]

Mercury diazoacetic ester reacts very little with methyl iodide even at 120°.[248]

α-Mercury dinaphthyl is unchanged after heating with ethyl iodide several hours at 160°.[249]

Thiophene mercuric chlorides do not react with alkyl halides or with halogen esters.[250]

When an alkyl halide reacts with a compound obtained from mercuric salts and an unsaturated compound it usually gives the original unsaturated compound. Thus ethanol mercuric iodide when heated with methyl iodide gives mercuric iodide, *ethylene,* and methyl alcohol. The same substance heated with chloroform at 150° gives mercuric

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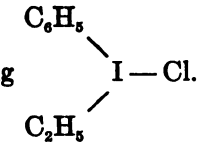
[241] Sulda, *Monatsh.* 1 (1880), 714.
[242] *Ibid.* 716.
[243] Sell and Lippmann, *J. prakt. Chem.* (1) 99 (1866), 432.
[244] Sakurai, *J. Chem. Soc.* 39 (1881), 487.
[245] Hofmann, *Ber.* 33 (1900), 1335.
[246] Dreher and Otto, *Ann.* 154 (1870), 128.
[247] Schoeller and Schrauth, *Ber.* 41 (1908), 2090.
[248] Buchner, *Ber.* 28 (1895), 219.
[249] Otto and Möries, *Ann.* 147 (1868), 178.
[250] Volhard, *Ann.* 267 (1892), 174.

iodide and chloride and a "non-gaseous unsaturated compound."[251] Di-epi-iodohydrine di-mercuric iodide obtained from allyl alcohol can be crystallized unchanged from hot benzyl chloride.[252] The mercury compound obtained from allylene reacts with ethyl iodide at 100° giving a variety of products among others, mercuric iodide, ethyl chloride, and ethyl ether.[253]

The mercurated formic esters obtained from carbon monoxide and alcoholic solutions of mercuric acetate react with methyl or n-propyl iodide at 100° giving carbon monoxide, mercuric iodide, and an alcohol.[254] This reaction is hard to understand if the structure of these substances is as indicated. On the other hand, the fact that these iodides do not give higher esters is no evidence against the structure formula as organic mercury compounds do not react with alkyl halides to give lengthened carbon chains.

Methyl iodide reacts normally with mercurated anilines forming the corresponding quarternary ammonium compounds.[255]

Methyl iodide also reacts normally with the sodium compounds of mercurated phenols giving the corresponding mercurated anisoles.[256]

Phenyl iodidechloride, $C_6H_5ICl_2$, reacts with organic mercury compounds as if dissociated into phenyl iodide and chlorine. Thus mercury diethyl gives ethyl mercuric chloride, ethyl chloride, and phenyl iodide.[257] In the presence of metallic sodium the reaction takes a different course giving 

X. Reaction with Acid Halides.

Organomercuric halides might be expected to react with acid halides forming mercuric halides and ketones. As with alkyl halides this reaction fails with practically all organic mercury compounds. The only mercury compounds which give ketones with acid chlorides are the

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[251] Hofmann and Sand, *Ber.* 33 (1900), 1349.

[252] Sand, *Ber.* 34 (1901), 1393.

[253] Kutscheroff, *Ber.* 17 (1884), 21.

[254] Manchot, *Ber.* 53 (1920), 984.

[255] Pesci, *Gazz. chim. ital.* 23 II (1893), 532, 537. Ruspaggiari, *Ibid.* 546. *Chem. Zentr.* 1894 I 501. Pesci, *Z. anorg. Chem.* 15 (1897), 219.

[256] Dimroth, *Ber.* 32 (1899), 764.

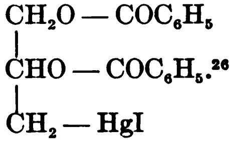
[257] Willgerodt, *Ber.* 30 (1897), 57; 31 (1898), 921.

α-mono-mercurated thiophenes. These react with acetyl chloride and benzoyl chloride forming acetthienone and thiophene phenyl ketone.[258] The reaction with acetyl chloride is likely to become violent. The best yield of the ketone is obtained by using thiophene, acetyl chloride, and a small amount of the α-thiophene mercuric chloride as a catalyst. In some cases this process gives a better yield than the Friedel-Crafts reaction. The mercurated thiophenes do not react with succinyl chloride or phosgene. The dimercurated thiophenes do not react with any acid chloride.

Allyl mercuric iodide does not react with acetyl or benzoyl chloride even on heating.[259] Mercury malonic ester gives no mercuric chloride even on long boiling with acetyl chloride.[260]

Mercury compounds containing amino or hydroxyl groups can be acylated without affecting the mercury. A number of mercurated anilines have been acetylated.[261] The ortho and para mercurated phenols can be acetylated by cold acetyl chloride.[262] o-Chloromercuridinitrophenol does not give an acetyl derivative but gives a small yield of a benzoyl derivative by the Schotten-Baumann reaction.[263]

The mercury addition products of ethylene compounds can be benzoylated. Thus ethanolmercuric iodide obtained from ethylene gives a benzoate, $IHg - CH_2 - CH_2O - COC_6H_5$.[264] Propylene glycol mercuric iodide, prepared from allyl alcohol, gives a dibenzoyl derivative,



$$\begin{array}{l} CH_2O - COC_6H_5 \\ | \\ CHO - COC_6H_5. \\ | \\ CH_2 - HgI \end{array}$$[265]

When the aromatic sulfonyl chlorides react with organic mercury compounds they give little or none of the expected sulfones. Thus mercury diphenyl heated with benzene sulfonyl chloride in benzene solution at 160° gives a complicated reaction. Small amounts of phenyl

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[258] Volhard, *Ann.* 267 (1892), 178. Steinkopf and Bauermeister, *Ann.* 403 (1914), 58.

[259] Oppenheim, *Ber* 4 (1871), 671.

[260] Schoeller and Schrauth, *Ber.* 41 (1908), 2090.

[261] Dimroth, *Ber.* 35 (1902), 2040. J. Rother, *Dissert.*, Berlin, 1911, pp. 45 & 58. Schoeller, Schrauth, and Rother, *Ber.* 45 (1912), 2817. Vecchiotti, *Gazz. chim. ital.* 44 II (1914), 37. *Chem. Zentr.* 1914 II 1350.

[262] Whitmore and Middleton, *J. Am. Chem. Soc.* 43 (1921), 619.

[263] Hantzsch and Auld, *Ber.* 39 (1906), 1113.

[264] Sand, *Ber.* 34 (1901), 1390.

[265] *Ibid.* 1393.

mercuric chloride and diphenyl sulfone are obtained.[266] Mercury diphenyl heated with p-toluene sulfonyl chloride at 120° for fifteen hours gives an almost quantitative yield of p-tolyl mercuric chloride and a mere trace of a sulfone.[267] The sulfonyl chlorides do not react with the mercurated thiophenes, as do the acyl chlorides.[268]

The reaction of the sulfide of o-mercuribenzoyl chloride with methyl alcohol has already been discussed under section III.[269]

Two compounds, the action of which may be considered here, are chloroformic ester and chlorocyanogen. The former of these substances gives "no satisfactory result" with mercury di-p-cymene and the latter gives no action at all.[270] Chloroformic ester reacts in the cold with mercury diazoacetic ester giving mercurous chloride and a thick oil which liberates nitrogen on treatment with an acid.[271] The mercurated thiophenes give no action when heated in a sealed tube with cyanogen chloride.[272]

XI. Reaction with Metals.

Mercury dialkyls and diaryls react with many metals on heating, giving organic compounds of these metals. In some cases the metal does not enter the reaction and the only change is a thermal decomposition of the mercury compound giving metallic mercury and a hydrocarbon according to the equation,

$$R_2Hg \text{ heated } = Hg + R - R.$$

The metals which behave in this way are copper, silver, gold and iron.[273]

The reaction of sodium with compounds of the type $R - Hg - Cl$ has already been mentioned in section IV under methods of making R_2Hg.[274] Sodium reacts with mercury dimethyl, diethyl, and diphenyl giving the corresponding sodium organic compounds.[275] The reaction

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[266] Otto, *Ber.* 18 (1885), 246.

[267] Otto, loc. cit. 249.

[268] Steinkopf and Bauermeister, *Ann.* 403 (1914), 59.

[269] Sachs, *Ber.* 53 (1920), 1740.

[270] Paterno and Colombo, *Ber.* 10 (1877), 1749.

[271] Buchner, *Ber.* 28 (1895), 219.

[272] Volhard, *Ann.* 267 (1892), 175.

[273] Frankland and Duppa, *J. Chem. Soc.* 17 (1864), 36. *Ann* 130 (1864), 125. Otto and Möries, *Ann.* 147 (1868), 179. Dreher and Otto, *Ann.* 154 (1870), 129.

[274] Steinkopf and Bauermeister, loc. cit. 57. Steinkopf, *Ann.* 413 (1917), 328.

[275] Buckton, *J. prakt. Chem.* (1) 79 (1860), 107. Chapman, *J. Chem. Soc.* 19 (1866), 150. Dreher and Otto, *Ann.* 154 (1870), 116 and 129. Acree, *Am. Chem. J.* 29 (1903), 588. Schorigin, *Ber.* 41 (1908), 2719. Hilpert and Grüttner, *Ber.* 46 (1913) 1679.

of mercury diethyl with sodium has been used in making sodium ethyl for use in synthetic work.[276]

Beryllium (glucinum) reacts with mercury diethyl and dipropyl giving the corresponding beryllium dialkyls.[277] Magnesium gives similar reactions with mercury methyl and phenyl.[278]

The action of zinc with mercury compounds has been studied more carefully than that of any other metal. It gives zinc dialkyls and diaryls readily. In fact the best method of making many organic zinc compounds is to make the mercury compound first and then heat it with zinc.[279] The mercury compounds which have been found to react with zinc are those of the following groups: (a) Methyl and ethyl,[280] (b) n-Propyl,[281] (c) Isobutyl,[282] (d) Isoamyl,[283] (e) Phenyl.[284]

α-Mercury dinaphthyl in carbon disulfide does not react with zinc in the cold.[285]

Cadmium reacts with mercury dimethyl, diethyl, and diphenyl at a high temperature giving some thermal decomposition and a partial formation of cadmium organic compounds.[286]

Aluminum reacts with mercury dimethyl, diethyl, and dipropyl giving the corresponding aluminum trialkyls.[287] It reacts vigorously with mercury diphenyl giving aluminum triphenyl.[288]

Bismuth reacts with mercury diethyl and diphenyl giving a partial transformation into the bismuth ethyl and phenyl compounds.[289]

[276] Schorigin, *Ber.* 41 (1908), 2723; 43 (1910), 1938.

[277] Cahours, *Compt. rend.* 76 (1873), 1383.

[278] Fleck, *Ann.* 276 (1893), 130. Hilpert and Grüttner, loc. cit. 1677.

[279] Frankland and Duppa, *J. Chem. Soc.* 17 (1864), 30. Marquardt, *Ber.* 21 (1888), 2038.

[280] Frankland and Duppa, *Ann.* 130 (1864), 118. *J. Chem. Soc.* 17 (1864), 29. Chapman, *J. Chem. Soc.* 19 (1866), 150. Löhr, *Ann.* 261 (1891), 75.

[281] Cahours, *Compt. rend.* 76 (1873), 751. *Ber.* 6 (1873), 568.

[282] Cahours, *J. prakt. Chem.* (2) 8 (1873), 398.

[283] Frankland and Duppa, loc. cit.

[284] Hilpert and Grüttner, *Ber.* 46 (1913), 1675. Dreher and Otto, *Ann.* 154 (1870), 129.

[285] Otto and Möries, *Ann.* 147 (1868), 179.

[286] Frankland and Duppa, loc. cit. 125 and 36. Löhr, loc. cit. 61. Hilpert and Grüttner, loc. cit. 1675.

[287] Buckton and Odling, *Ann. Spl.* 4 (1865), 110 ff. Cahours, *Compt. rend.* 76 (1873), 135, 752. *Ber.* 6 (1873), 568.

[288] Hilpert and Grüttner, *Ber.* 45 (1912), 2829.

[289] Hilpert and Grüttner, *Ber.* 46 (1913), 1675. Frankland and Duppa, loc. cit. 125 and 36.

Chapter IV.

Alkyl Mercury Compounds.

Methyl Mercury Compounds.

Mercury Dimethyl.

Preparation.

1. From methyl iodide and sodium amalgam.[1] Methyl iodide does not react with sodium amalgam at ordinary temperatures even on long standing. As soon as a little ethyl or methyl acetate is added reaction starts with a considerable evolution of heat. The catalytic action of the ester is not understood.

Ten parts of methyl iodide and one part of methyl acetate are treated in the cold with an excess of dilute sodium amalgam (about 1 : 500). The flask must be provided with an efficient upright condenser and usually must be cooled during the more violent part of the reaction. The reaction is complete when a sample tested with nitric acid gives no iodine. If the mixture becomes too thick from the separation of sodium iodide it may be distilled from the water bath and the distillate may be treated with fresh amalgam. At the end of the reaction the methyl acetate is distilled off for use in later runs. The residue is treated with water and distilled from an oil bath at a temperature not above 110°. The distillate consists of two layers. The lower layer is shaken with concentrated potassium hydroxide to remove traces of methyl acetate and then washed with water and distilled. B.P. 93-96°.

2. From methyl mercuric iodide and zinc dimethyl.[2]

3. From methyl mercuric iodide and potassium cyanide.[3]

A mixture of the solids is subjected to dry distillation. The distil-

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[1] Frankland and Duppa, *J. Chem. Soc.* 16 (1863), 415. *Ann.* 130 (1864), 117. Otto, *Ann.* 154 (1870), 198. L. W. Jones, *J. Am. Chem. Soc.* 40 (1918), 1271.

[2] Buckton, *Ann.* 109 (1859), 219. *J. prakt. Chem.* (1) 76 (1859), 362.

[3] Buckton, *Ann.* 109 (1859), 218. *Ann.* 108 (1858), 103.

late is washed with water, dried with calcium chloride, and redistilled. Yield poor.

4. From methyl mercuric iodide distilled with a base.[4]

Potassium hydroxide or calcium hydroxide may be used. The yield is even poorer than by the cyanide method.

5. From mercuric chloride and aluminum carbide.[5]

A mixture of equal weights of the substances is added to water and the mixture is kept slightly acid by the careful addition of hydrochloric acid. Drops of mercury dimethyl soon separate.

6. From mercuric chloride and methyl magnesium iodide.[6]

Properties.[7]

Mercury dimethyl is a colorless, strongly refractive liquid with a slight sweetish odor. It is easily inflammable. It is easily soluble in alcohol and ether. Its alcoholic solution is precipitated by the addition of water. B.P. 93-96°. Sp.g. 3.069. Vapor density referred to air 8.29. It crystallizes at the temperature of evaporating solid carbon dioxide. It easily dissolves caoutchouc, resins, and phosphorus but dissolves sulfur only slightly. It is a very deadly poison.[8]

Reactions.

1. With halogens.[9]

An alcoholic solution reacts with iodine forming methyl iodide and methyl mercuric iodide. It reacts in a similar way with bromine.

2. With iodocyanogen.[10]

An ether solution at 50° gives mercuric cyanide. At 110° the products are mercuric iodide and methyl isocyanide.

3. With metals.

Sodium reacts with an alcoholic solution giving metallic mercury.[11] In inert solvents sodium forms sodium methyl.[12] An ether solution

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[4] Buckton, *Ann.* 103 (1858), 104.

[5] Hilpert and Ditmar, *Ber.* 46 (1913), 3738.

[6] Private communication from C. S. Marvel of the University of Illinois. Yield about 60 per cent.

[7] Buckton, loc. cit. Seidel, *J. prakt. Chem.* (2) 29 (1884), 135. Hilpert and Ditmar, loc. cit. Crymble, *J. Chem. Soc.* 105 (1914), 658. Löhr, *Ann.* 261 (1891), 59.

[8] Schoeller, Schrauth, and Müller, *Biochem. Z.* 33 (1911), 381. Hilpert and Ditmar, loc. cit. 3741.

[9] Frankland and Duppa, *J. Chem. Soc.* 16 (1863), 415. *Ann.* 130 (1864), 104. Buckton, *Ann.* 108 (1858), 103. Hilpert and Ditmar, loc. cit. 3740.

[10] Calmels, *Compt. rend.* 99 (1884), 240.

[11] Chapman, *J. Chem. Soc.* 19 (1866), 150. *Ann.* 139 (1866), 128.

[12] Schlenk, *Ber.* 50 (1917), 262.

treated with sodium and carbon dioxide gives a very small yield of sodium acetate.[13]

Magnesium does not react with mercury dimethyl up to 120°. If heated for 36 hours at 130° it gives solid magnesium dimethyl and metallic mercury.[14]

Zinc at 120° gives zinc dimethyl.[15]

Cadmium gives no cadmium organic compounds but only cadmium amalgam and ethane.[16]

Aluminum forms aluminum trimethyl.[17]

4. With cadmium iodide.[18]

Heating a mixture of mercury dimethyl and cadmium iodide gives a very little mercuric iodide, mercury, and ethane. No organic cadmium compound is obtained.

5. With acids.[19]

Concentrated sulfuric acid and hydrochloric acid give methane and the corresponding methyl mercuric salts.

Glacial acetic acid at 250° removes one methyl group as methane. The other products are metallic mercury and a brown amorphous substance. This reaction differs from that of mercury di-isoamyl and mercury dibenzyl which give isoamyl acetate and benzyl acetate respectively.[20]

6. With stannous chloride.[21]

A crystalline compound is formed. Water decomposes it giving methyl mercuric chloride and a soluble tin compound.

7. With phosphorus trichloride.[22]

Methyl mercuric chloride is the only product isolated.

8. With antimony trichloride.[23]

The reaction takes place according to the equation,

$$2(CH_3)_2Hg + SbCl_3 \rightarrow (CH_3)_3SbCl_2 + CH_3HgCl + Hg.$$

The process involves a peculiar oxidation of the antimony and reduction of the mercury.

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[13] Schorigin, *Ber.* 41 (1908), 2717.
[14] Löhr, *Ann.* 261 (1891), 48. Fleck, *Ann.* 276 (1893), 130.
[15] Frankland and Duppa, *Ann.* 130 (1864), 117. *J. Chem. Soc.* 17 (1864), 28.
[16] Löhr, loc. cit.
[17] Buckton and Odling, *Ann. Spl.* 4 (1865), 110.
[18] Löhr, loc. cit.
[19] Buckton, *Ann.* 108 (1858), 105.
[20] L. W. Jones, *J. Am. Chem. Soc.* 40 (1918), 1271. *Chem. Abst.* 12 (1918), 2320.
[21] Buckton, loc. cit.
[22] Buckton, loc. cit.
[23] Landolt, *Ann.* 78 (1851), 91.

9. With nitrogen peroxide.[24]

Imidodihydroximic acid is probably formed. The reaction differs from that of the aromatic mercury compounds in not giving any diazonium salts.

10. With potassium permanganate.[25]

The permanganate is reduced to manganese dioxide giving a product which reacts with hydrochloric acid to form methyl mercuric chloride. The intermediate product is probably methyl mercuric hydroxide.

11. With mercuric salts.[26]

Mercuric iodide readily reacts with mercury dimethyl giving methyl mercuric iodide.

Isolation of the complex metal, CH_3Hg —.[27]

Methyl mercuric halides electrolyzed in liquid ammonia solution give a fine black deposit on the cathode. This deposit is a good conductor of electricity but does not amalgamate with mercury. When allowed to come to room temperature it decomposes suddenly with evolution of heat, forming mercury and mercury dimethyl. The free methyl mercury group can also be obtained as fine black flakes by electrolyzing a water or alcohol solution of methyl mercuric chloride.

The hydroxide and oxide of mercury methyl.[28]

A solution of the hydroxide is obtained by treating methyl mercuric iodide with silver oxide and water. The aqueous solution is strongly basic. Treatment of methyl mercuric iodide with potassium hydroxide gives a solid "methyl mercuric oxide" which is soluble in an excess of base. The hydroxide is also formed when potassium permanganate acts on mercury dimethyl.

Methyl mercuric chloride.[29]

Preparation.

1. From the action of hydrochloric acid on mercury dimethyl. The other product is methane gas.[30]

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[24] **Bamberger, *Ber.* 32 (1899), 3546. *Cf. Chem. Zentr.* 1898 II 1015.**

[25] **Seidel, *J. prakt. Chem.* (2) 29 (1884), 134 and 136.**

[26] **Buckton, loc. cit.**

[27] **Kraus, *J. Am. Chem. Soc.* 35 (1913), 1740.**

[28] **Frankland, *Ann.* 85 (1853), 363. Dünhaupt, *Ann.* 92 (1854), 381. *J. prakt. Chem.* (1) 61 (1854), 399. Crymble, *J. Chem. Soc.* 105 (1914), 666.**

[29] **Crymble, *Ibid.* 668.**

[30] **Buckton, *Ann.* 108 (1858), 105.**

2. From the action of water on the crystalline compound of stannous chloride with mercury dimethyl.[31]

3. From mercury dimethyl and phosphorus trichloride.[32]

4. From the action of hydrochloric acid on methyl mercuric hydroxide obtained by oxidizing mercury dimethyl with potassium permanganate.[33]

5. From aluminum carbide treated with an excess of mercuric chloride and an excess of 10 per cent hydrochloric acid. Yield 30 per cent.[34]

6. Probably the best methods of preparation would be: (a) treatment of methyl magnesium iodide with a large excess of mercuric chloride, or (b) treatment of mercury dimethyl prepared by the sodium amalgam method with the calculated amount of mercuric chloride in alcohol.

Properties.[35]

White crystals. M.P. 170°. Volatile with steam. Peculiar disagreeable odor. (CHHgCl.) [36] Density 4.063. It absorbs light less than ethyl mercuric chloride which in turn absorbs it less than mercuric chloride. The molecular weight determined in methyl sulfide and in ethyl sulfide is normal.

Methyl mercuric bromide. M.P. 160°.[37]

Methyl mercuric iodide.[38]

Preparation.

1. From mercury dimethyl and iodine in alcohol.[39]

2. From methyl iodide and mercury. A mixture of the calculated

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[31] *Ibid.*

[32] *Ibid.*

[33] Seidel, *J. prakt. Chem.* (2) 29 (1884), 135.

[34] Hilpert and Ditmar, *Ber.* 46 (1913), 3739.

[35] Schröder, *Ber.* 12 (1879), 563. Ley and Fischer, *Z. anorg. Chem.* 82 (1913), 338. Crymble, *J. Chem. Soc.* 105 (1914), 658. Weiner, *Z. anorg. Chem.* 15 (1897), 37.

[36] The analyses of the compounds mentioned will be indicated by parentheses enclosing the symbols of the substances determined in the analyses. If no comment is made it will be understood that the analyses check with the theoretical values within reasonable limits. Any unusual variations will be indicated.

[37] Crymble, *Ibid.*

[38] Frankland and Duppa, *Ann.* 130 (1864), 107. *J. Chem. Soc.* 16 (1863), 415. Crymble, *Ibid.*

[39] Buckton, loc. cit. 103. Frankland and Duppa, loc. cit. 416. Hilpert and Ditmar, loc. cit.

amounts of these substances turns to a crystalline mass when allowed to stand in direct sunlight for about sixty hours.[40]

3. From a water solution of the chloride and potassium iodide.[41]

Properties.

Colorless pearly leaflets. It is best crystallized from hot methyl alcohol in which it is much more soluble than in ether or ethyl alcohol. It is insoluble in water, soluble in ether and in methyl iodide. It is slightly volatile and has a slight but peculiar disagreeable odor. M.P. 145° (143°). (CHHgI.)

Methyl mercuric iodide adds to $(CH_3)_2SI_2$ giving the same product as is obtained from $(CH_3)_3SI$ and HgI_2.[42]

Methyl mercuric acetate.[43]

Mercury dimethyl and glacial acetic acid heated in a sealed tube for one hour at 120° give methane and the acetate. The latter is purified by crystallization from hot acetic acid. Satiny rhombic leaflets. It has a peculiar disagreeable odor and is practically insoluble in boiling water and cold acetic acid. It is more soluble in hot acetic acid and in alcohol. It is volatile with steam. M.P. 142-3°. *Note.* It is probable that the substance prepared by Otto was not the pure acetate. The substance prepared from methyl mercuric iodide and silver acetate has different properties from those given by Otto.[44]

Methyl mercuric nitrate.[45]

The filtrate from the action of silver nitrate on methyl mercuric iodide gives colorless leaflets of the nitrate. It is very soluble in water but less so in alcohol. It melts to a colorless liquid at 100°. Its solution gives no precipitate with base solutions. A solution treated with hydrochloric acid or a chloride solution gives a precipitate of methyl mercuric chloride.

Methyl mercuric sulfate.[46]

Prepared from mercury dimethyl and concentrated sulfuric acid.

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[40] Frankland, *Ann.* 85 (1853), 361.

[41] Hilpert and Ditmar, loc. cit. 3740.

[42] Smiles, *J. Chem. Soc.* 77 (1900), 162; 91 (1907), 1394.

[43] Otto, *Ann.* 154 (1870), 199.

[44] Unpublished results obtained by M. C. Sneed and J. L. Maynard of the University of Minnesota.

[45] Strecker, *Ann.* 92 (1854), 79.

[46] Buckton, *Ann.* 108 (1858), 105.

Methyl mercuric sulfide.[47]

An excess of methyl mercuric iodide in an excess of base reacts with ammonium sulfide giving a slightly yellow flocculent precipitate. It has a peculiar unbearable odor. It may also be prepared from a solution of methyl mercuric chloride in 10 per cent hydrochloric acid treated with hydrogen sulfide. Warming changes the methyl mercuric sulfide to mercuric sulfide and mercury dimethyl. (S, low.) [48]

Ethyl Mercuric Compounds

Mercury Diethyl.

Preparation.

1. From zinc diethyl and dry mercuric chloride.[49]

The mixture of the two substances has to be cooled at first to abate the violence of the reaction. When the reaction slackens the mixture is warmed gently and then distilled. Water is added to decompose any unchanged zinc compound.

2. From zinc diethyl and ethyl mercuric iodide.[50]

The latter substance is prepared from ethyl iodide and mercury in diffused sunlight. It is dissolved in zinc diethyl. The solution on standing soon deposits zinc iodide. The mercury diethyl is then distilled off.

3. From zinc diethyl and mercurous chloride.[51]

4. From ethyl iodide and sodium amalgam.[52]

The preparation is carried out exactly as in the case of the methyl compound except that ethyl acetate is used as the catalyst and the mixture is warmed slightly.

5. From ethyl bromide and sodium amalgam.[53]

The bomide acts as well as the iodide.

6. From allyl mercuric iodide and zinc diethyl.[54]

These substances react in *cold* ether solution forming mercury,

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[47] Frankland, *Ann.* 85 (1853), 363. Hilpert and Ditmar, *Ber.* 46 (1913), 3740.

[48] When an analysis varies widely from the theoretical value the direction of the variation will be indicated.

[49] Buckton, *Ann.* 109 (1859), 219. *J. prakt. Chem.* (1) 76 (1859), 362.

[50] Buckton, loc. cit. 222.

[51] Buckton, loc. cit. 221.

[52] Frankland and Duppa, *J. Chem. Soc.* 16 (1863), 418. *Ann.* 130 (1864), 104. Otto, *Ann.* 154 (1870), 198. Hale and Nunez, *J. Am. Chem. Soc.* 33 (1911), 1561. L. W. Jones, *J. Am. Chem. Soc.* 40 (1918), 1270. *Chem. Abst.* 12 (1918), 2320.

[53] Chapman, *J. Chem. Soc.* 19 (1866), 150. *Ann.* 139 (1866), 128.

[54] Oppenheim, *Ber.* 4 (1871), 671.

mercury diethyl, zinc iodide, and diallyl. This reaction is hard to explain unless allyl mercuric iodide here undergoes the decomposition which ordinarily takes place only at high temperatures giving diallyl, mercury, and mercuric iodide which then reacts with the zinc diethyl.[55]

7. From methyl mercuric iodide and zinc diethyl.[56]

Distillation of these substances appears to give mercury diethyl and zinc dimethyl. This reaction should be contrasted with the action of ethyl mercuric chloride with zinc dimethyl which is believed to give the mixed mercury alkyl, ethyl mercury methyl.

8. From α-naphthyl mercuric bromide and ethyl magnesium bromide.[57]

Here the mixed compound, ethyl mercury naphthyl would be expected but is not obtained. Perhaps it is formed and then separates into mercury diethyl and mercury dinaphthyl.

9. From ethyl mercuric iodide and potassium cyanide.[58]

The dry distillation of these substances gives a poor yield.

10. By the oxidation of ethyl hydrazine by mercuric oxide.[59]

11. From bismuth triethyl and mercuric chloride.[60]

Properties.[61]

Mercury diethyl is a colorless liquid with a slight hazel odor. B.P. 159°. It is almost insoluble in water, only slightly soluble in alcohol, but readily soluble in ether. Sp. g. 2.44. (CHHg.) At low temperatures it turns to a thick viscous liquid. It burns readily but with a less luminous flame than the methyl compound. Exposed to sunlight it deposits a white waxy substance which is soluble in ether and in hot alcohol. Heating decomposes it to mercury, a combustible gas, and a black carbonaceous residue. The waxy substance has a strong disagreeable odor resembling garlic. When applied to the skin it causes burns which are slow to heal.[62] When the vapor of mercury diethyl is heated a little above 205° it decomposes with a slight explosion forming mercury and an inflammable gas. Mercury diethyl is one of the

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[55] Linnemann, *Ann.* 140 (1866), 180.

[56] Frankland, *Ann.* 111 (1859), 57.

[57] Hilpert and Grüttner, *Ber.* 48 (1915), 908.

[58] Buckton, *Ann.* 108 (1858), 105.

[59] E. Fischer, *Ann.* 199 (1879), 332.

[60] Dünhaupt, *J. prakt. Chem.* (1) 61 (1854), 423. *Ann.* 92 (1854), 379.

[61] Hale and Nunez, loc. cit. Frankland and Duppa, loc. cit. Buckton, loc. cit. Crymble, loc. cit. Löhr, *Ann.* 261 (1891), 59.

[62] Hale and Nunez, loc. cit. 1561.

deadliest poisons.[63] Given in less than lethal doses it can be detected in the organs of animals months after its administration.[64]

Reactions.

1. With halogens.[65]

Mercury diethyl dropped into chlorine gas catches fire. Treatment with iodine or bromine and water gives the corresponding ethyl mercuric halide.

2. With metals.[66]

Sodium in alcohol gives metallic mercury. Sodium acts with pure mercury diethyl giving a gray solid which is spontaneously inflammable. This gray solid is probably impure sodium ethyl. On warming it gives a mixture of ethane and ethylene.

Carbon dioxide acting on mercury diethyl and sodium in benzene gives a 12 per cent yield of sodium benzoate. With toluene the product is phenyl acetic acid. Similar reactions have been carried out with m-xylene, ethyl benzene, benzophenone, methyl benzoate, benzaldehyde, p-cymene, and thiophene. The hydrocarbons apparently act with the sodium ethyl giving sodium derivatives which then react with the carbon dioxide.[67]

Magnesium yields magnesium diethyl and mercury. The solid magnesium compound is even more inflammable than the corresponding methyl compound.

Zinc heated with mercury diethyl for 36 hours at 100° acts more readily than it does with the methyl compound. It forms zinc diethyl.

Cadmium reacts slowly on heating giving only a partial change to cadmium diethyl.

Aluminum reacts at the temperature of the water bath giving aluminum triethyl.

Iron in the form of the reduced powder gives no action until heated hot enough to give a thermal decomposition of the mercury diethyl forming mercury and butane. No iron carbon compound is obtained.

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[63] Forster, *J. Chem. Soc.* 117 (1920), 1158.

[64] Schoeller, Schrauth, and Müller, *Biochem. Z.* 33 (1911), 403.

[65] Chapman, *J. Chem. Soc.* 19 (1866), 150. *Ann.* 139 (1866), 128. Buckton, *Ann.* 112 (1859), 222.

[66] Buckton, *J. prakt. Chem.* (1) 79 (1860), 107. Frankland and Duppa, *Ann.* 130 (1864), 120. *J. Chem. Soc.* 17 (1864) 31. Buckton and Odling, *Ann. Spl.* 4 (1865), 110. Cahours, *Compt. rend.* 76 (1873), 135 and 1384. *Jahresber.* (1873) 517. Schorigin, *Ber.* 41 (1908), 2719 and 2725; 43 (1910), 1931. Zeiser, *Ber.* 28 (1895), 1675. Peters, *Ber.* 41 (1908), 3174.

[67] Schorigin, loc. cit.

Copper behaves the same as iron.

Beryllium gives beryllium diethyl.

Bismuth heated with mercury diethyl at 140° gives large amounts of bismuth triethyl but the reaction cannot be brought to completion.

Silver and *gold* cause only a thermal decomposition of the mercury diethyl.

Zirconium gives no carbon compound even at 200°.

Tellurium gives diethyl telluride.

3. With acids.[68]

Mercury diethyl does not react with dilute acids. With concentrated hydrochloric or sulfuric acid it yields ethane and a salt of mercury ethyl. This method has been recommended for the preparation of pure ethane.

Mercury diethyl heated with glacial acetic acid at 190° gives ethane, ethylene, metallic mercury, and some ethyl acetate.[69]

4. With bromoacetic ester.[70]

Refluxing the two liquids at 150° gives a small amount of a gas which unites with bromine and is probably ethylene. After refluxing for 8 hours the mixture is cooled. Crystals of ethyl mercuric bromide separate. The mother liquor gives some ethyl acetate. The reaction can probably be represented by the equation

$$C_2H_5 - Hg - C_2H_5 + Br - CH_2 - CO_2Et \rightarrow$$
$$CH_2 = CH_2 + C_2H_5 - Hg - Br + CH_3 - CO_2Et.$$

No explanation of the reaction has been suggested.

5. With potassium permanganate.[71]

Heating mercury diethyl with aqueous potassium permanganate gives manganese dioxide and a strongly basic solution which probably contains ethyl mercuric hydroxide. Hydrochloric acid precipitates ethyl mercuric chloride from this solution.

6. With allyl iodide.[72]

Equal molecules of the substances heated in a sealed tube for two days at 130° yield ethyl mercuric iodide, ethyl iodide, and diallyl. Apparently the high temperature causes the allyl iodide to give diallyl

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[68] Buckton, *Ann.* 112 (1859), 221. *J. prakt. Chem.* (1) 79 (1860), 107. Schorlemmer, *Ann.* 132 (1864), 234.

[69] L. W. Jones, *J. Am. Chem. Soc.* 40 (1918), 1271. *Chem. Abst.* 12 (1918), 2320.

[70] Sell and Lippmann, *J. prakt. Chem.* (1) 99 (1866), 432.

[71] Seidel, *J. prakt Chem.* (2) 29 (1884), 134.

[72] Suida, *Monatsh.* 1 (1880), 714.

and iodine which immediately reacts with the mercury diethyl giving the observed products.

7. With iodoform.[73]

The reaction starts at 70°, becomes rapid at 90°, and is complete at 105°. Higher temperatures make it too rapid. The products are acetylene, identified by the copper and silver compounds ethylene, identified by the formation of ethylene dibromide; and ethyl iodide and ethyl mercuric iodide. The formation of ethylene is not very satisfactorily explained by the equation,

$$2CHI_3 + 4(C_2H_5)_2Hg = 4C_2H_5 - Hg - I + 2C_2H_5I + 3C_2H_4.$$

8. With arsenic trichloride.[74]

The products are ethyl dichloroarsine and ethyl mercuric chloride.

9. With phenyl arsenious sulfide.[75]

The reaction takes place on heating according to the equation,

$$(C_2H_5)_2Hg + C_6H_5AsS = HgS + C_6H_5As(C_2H_5)_2.$$

10. With arsenobenzene.[76]

When the substances are heated to 150° phenyldiethyl arsine and metallic mercury are formed.

11. With aromatic iodide-chlorides.[77]

When phenyl iodide-chloride, $C_6H_5ICl_2$, is warmed gently with mercury diethyl a violent reaction takes place. The reaction does not give the desired product, ethyl phenyl iodonium chloride, but gives phenyl iodide, ethyl chloride, and ethyl mercuric chloride. The iodide-chloride apparently dissociates into phenyl iodide and chlorine and the latter reacts with the mercury diethyl. When a mixture of phenyl iodide-chloride and mercury diethyl is treated with metallic sodium the product is ethyl phenyl iodonium chloride. In this case the real reacting substance is probably sodium ethyl.

12. With mercuric salts.[78]

Alcoholic mercuric chloride gives ethyl mercuric chloride.

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[73] Suida, loc. cit. 723.

[74] La Coste, *Ann.* 208 (1881), 83.

[75] Michaelis and Schulte, *Ber.* 15 (1882), 1956.

[76] Michaelis and Schulte, loc. cit. and *Ber.* 14 (1881), 913.

[77] Willgerodt, *Ber.* 30 (1897), 57; 31 (1898), 921.

[78] Frankland and Duppa, *Ann.* 111 (1859), 59; 130 (1864), 109. *J. Chem. Soc.* 16 (1863), 415.

The complex metal, C_2H_5Hg—.[79]

This substance is obtained by electrolysis in the same way as the methyl compound. On being compressed by rubbing with a glass rod it takes on a coppery appearance, thus differing from the methyl compound which gives no sign of metallic luster.

Ethyl mercuric hydroxide.[80]

A hot alcoholic solution of ethyl mercuric chloride reacts with silver oxide forming silver chloride and a solution of the base. Evaporation of the alcohol leaves a colorless oil. It is very soluble in alcohol and water giving a strongly basic solution. It burns the skin like caustic alkalies and causes blisters like cantharides. It reacts with ammonium salts liberating ammonia and forming the corresponding ethyl mercuric salts. Zinc acts on the pure substance giving zinc amalgam and zinc diethyl. It precipitates solutions of salts of zinc, copper, aluminum, iron, tin, gold, and platinum. Cupric and ferric solutions give precipitates differing from those given by ordinary bases. Hydrogen sufide gives a white precipitate which slowly blackens on standing. Hydrobromic acid and hydrocyanic acid react with the base forming salts. Bromine forms ethyl mercuric bromide and the corresponding bromate. Iodine forms ethyl mercuric iodide.

Ethyl mercuric chloride.

Preparation.

1. From zinc diethyl and an excess of mercuric chloride.[81]

2. From mercury diethyl and mercuric chloride.[82]

A mixture of the two substances in alcohol is heated to boiling and filtered hot. On cooling crystals separate. These are purified by dissolving in hot alcohol and precipitating by adding a little water.

3. From ethyl mercuric hydroxide obtained by oxidizing mercury diethyl by potassium permanganate.[83]

4. From the hydroxide and ammonium chloride solution.[84]

5. From bismuth triethyl and mercuric chloride.[85]

Mixing the alcoholic solutions gives an immediate precipitate of

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[79] Kraus, *J. Amer. Chem. Soc.* 35 (1913), 1737.

[80] Dünhaupt, *J. prakt. Chem.* (1) 61 (1854), 415. *Ann.* 92 (1854), 379.

[81] Buckton, *Ann.* 109 (1859), 219. *J. prakt. Chem.* (1) 76 (1859), 362. Frankland, *Ann.* 111 (1859) 59.

[82] Frankland and Duppa, *Ann.* 130 (1864), 109.

[83] Seidel, loc. cit.

[84] Dünhaupt, *J. prakt. Chem.* (1) 61 (1854), 428. *Ann.* 92 (1854), 379.

[85] *Ibid.* 415.

ethyl mercuric chloride. Ethyl bismuth dichloride remains in solution.

6. By precipitating a solution of ethyl mercuric nitrate with a chloride solution.[86]

Properties.[87]

Silvery iridescent leaflets. Difficultly soluble in cold alcohol, readily soluble hot, slightly soluble in ether, and practically insoluble in water. M.P. 192.5°. It sublimes easily even at 40° giving thin colorless leaflets. Density 3.5. It absorbs light less than mercuric chloride but more than methyl mercuric chloride. (CHHgCl.)

Ethyl mercuric chloride is more toxic than mercury diethyl. The latter substance probably changes to the chloride in the body.[88]

Reactions.

1. With zinc dimethyl. The product is possibly methyl mercury ethyl which decomposes on distillation giving the simple mercury alkyls.[89]

2. With phenyl iodide-chloride. No reaction takes place cold. On heating the products are phenyl iodide, ethyl chloride, and ethyl mercuric chloride. Thus the iodide-chloride acts the same as it does with mercury diethyl, that is, it acts like phenyl iodide and free chlorine.[90]

3. With metallic zinc forming ethyl zinc chloride.[91]

Ethyl mercuric bromide.[92]

Preparation.

1. From mercuric bromide and bismuth triethyl in alcoholic solution.

2. From ethyl mercuric hydroxide and hydrobromic acid or bromine.

3. From mercury diethyl and bromoacetic ester at 150°.

Properties.

Like those of the chloride. (Br.)

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[86] Strecker, *Ann.* 92 (1854), 78.

[87] Strecker, loc. cit. Dünhaupt, loc. cit. Seidel, loc. cit. Frankland and Duppa, loc. cit. Crymble, *J. Chem. Soc.* 105 (1914), 668. Schroeder, *Ber.* 12 (1879), 563. Ley and Fischer, *Z. anorg. Chem.* 82 (1913), 338.

[88] Schoeller, Schrauth, and Müller, *Biochem. Z.* 33 (1911), 405.

[89] Frankland, *Ann.* 111 (1859), 59.

[90] Willgerodt, *Ber.* 31 (1898), 921.

[91] Dünhaupt, loc. cit.

[92] Dünhaupt, loc. cit. Sell and Lippmann, *J. prakt. Chem.* (1) 99 (1866), 432.

Ethyl mercuric iodide.

Preparation.

1. From ethyl iodide and metallic mercury in diffused light.[93]
2. From an alcoholic solution of the hydroxide and iodine.[94]
3. From mercury diethyl and allyl iodide heated.[95]
4. From mercury diethyl heated with iodoform.[96]

Properties.[97]

Fine white leaflets having an unpleasant odor. It is best recrystallized from alcohol and ether. It can also be recrystallized from boiling ammonium hydroxide or potassium hydroxide. Exposure to sunlight turns it yellow and finally red with the formation of mercuric iodide. M.P. 182°. ($CHHgI$).

Reactions.[98]

1. Alcoholic silver nitrate gives a solution of ethyl mercuric nitrate.
2. Zinc diethyl changes it to mercury diethyl.
3. Dry distillation with potassium cyanide gives a poor yield of mercury diethyl.

Other ethyl mercuric salts.

The *cyanide* is prepared from the hydroxide and concentrated hydrocyanic acid. It forms good crystals which are very volatile and have a strong odor. It appears to be very toxic. The cyanide cannot be isolated from a mixture of alcoholic mercuric cyanide and bismuth triethyl although the repulsive odor of the mixture would indicate that some of it is formed.[99]

The *acetate* is prepared by heating mercury diethyl with glacial acetic acid in a sealed tube at 120° for one hour. It forms shiny rhombic leaflets, which can be recrystallized from hot acetic acid. Peculiar disagreeable odor. M.P. 178°.[100]

The *nitrate* can be made from alcoholic solutions of the iodide and

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[93] Frankland, *Ann.* 111 (1859), 59. Strecker, *Ann.* 92 (1854), 76. Buckton, *Ann.* 109 (1859), 222. *J. prakt. Chem.* (1) 76 (1859) 362.

[94] Dünhaupt, loc. cit.

[95] Suida, loc. cit.

[96] *Ibid.*

[97] Strecker, *Ann.* 92 (1854), 77. Dünhaupt, *J. prakt. Chem.* (1) 61 (1854), 425, *Ann.* 92 (1854), 379. Crymble, *J. Chem. Soc.* 105 (1914), 668.

[98] Strecker, loc. cit. Buckton, loc. cit.

[99] Dünhaupt, loc. cit.

[100] Otto, *Ann.* 154 (1870), 199.

silver nitrate. Evaporation of the filtrate in vacuo leaves clear prisms very soluble in alcohol but less so in water.[101] The nitrate can also be prepared from the hydroxide and nitric acid. Evaporation leaves an oil which crystallizes on standing. (CH,N_2O_5).[102] A solution of the nitrate in water reacts with chloride solutions giving a precipitate of ethyl mercuric chloride.

The *sulfate* can be made from alcoholic solutions of one of the halides and silver sulfate. Evaporation of the filtrate gives silvery leaflets. $(CHHg,SO_3)$.[103] The sulfate is also obtained by treating mercury diethyl with concentrated sulfuric acid.[104]

The *sulfide* is obtained by adding ammonium sulfide to an alcoholic solution of the chloride. The precipitate is soluble in an excess of the sulfide. When dried the precipitate forms a yellow powder which can be crystallized from ether. (CHSHg.)

The *phosphate* is obtained as a thick mass soluble in water by treating a dilute alcoholic solution of the chloride with silver phosphate and evaporating the filtrate.[105]

The *carbonate* and *oxalate* may be obtained in the same way as the phosphate. Both are crystalline.

n-Propyl Mercury Compounds.

Mercury Dipropyl.

Preparation.[106]

Normal propyl iodide treated with an excess of dilute sodium amalgam gives a pasty mass which is treated with alkali and distilled with steam. The heavy oil is separated, evaporated on the steam bath, and then distilled. B.P. 189-91°.

Properties.

Colorless mobile liquid. Almost odorless when cold but having a very penetrating odor when hot. It is almost insoluble in water, soluble in alcohol, and very soluble in ether. Its density at 16° is 2.124. B.P. 189-91°.

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[101] Strecker, loc. cit.
[102] Dünhaupt, loc. cit.
[103] Dünhaupt, loc. cit.
[104] Buckton, loc. cit.
[105] Dünhaupt, loc. cit.
[106] Cahours, *Compt. rend.* 76 (1873), 134. *Ber.* 6 (1873), 567. *Jahresb.* (1873), 517.

Reactions.

1. With halogens.[107]

Iodine reacts violently forming propyl iodide and propyl mercuric iodide or mercuric iodide depending on the amount used. Bromine water is decolorized at once giving shining plates of propyl mercuric bromide.

2. With acids.

It reacts with the following acids forming propane and the corresponding propyl mercuric salt: hydrochloric, sulfuric, nitric, and acetic acids.

3. With tripropyl stannic iodide it gives tin tetrapropyl.

4. With metals.[108]

Beryllium in a sealed tube at 130° quickly forms mercury and beryllium dipropyl. *Zinc* and *Aluminum* act in a similar way.

Propyl mercuric hydroxide.

When propyl mercuric iodide is treated with moist silver oxide an alkaline solution is obtained which on evaporation leaves a viscous mass which gives a few crystals on standing in a vacuum over sulfuric acid. A solution of the substance in water has strong basic properties. It forms salts with acids. Among the salts made in this way are the sulfate, nitrate, arsenate, tartrate, oxalate, and cyanide.

Propyl mercuric chloride.

A white crystalline substance obtained by boiling mercury dipropyl with hydrochloric acid or by treating a water solution of the base with hydrochloric acid. It can be recrystallized from hot alcohol.

Propyl mercuric bromide.

Shiny white plates obtained by treating mercury dipropyl with bromine water or by treating the base with hydrobromic acid.

Propyl mercuric iodide.

Treatment of mercury dipropyl with iodine in alcohol yields the iodide which crystallizes from hot alcohol in pearly scales having a very disagreeable odor. It reacts with moist silver oxide forming the hydroxide.

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[107] Cahours, loc. cit. and *Compt. rend.* 76 (1873), 749.

[108] Cahours, loc. cit. and *Compt. rend.* 76 (1873), 1383.

Other propyl mercuric salts.

The *cyanide* is obtained as an oily product from the action of hydrocyanic acid on the hydroxide. It has not been obtained pure. The *sulfate* is obtained as a white crystalline substance by treating the base with dilute sulfuric acid or the dialkyl compound with concentrated sulfuric acid. The *nitrate* is a crystalline substance prepared in the same ways as the sulfate. The *arsenate* is obtained as a white precipitate on mixing solutions of the base and arsenic acid. The *oxalate* and *tartrate* are obtained in the same way. The *acetate* is made by heating mercury dipropyl on the steam bath with acetic acid and diluting the resulting solution with water. The other product of the reaction is propane.

Isopropyl Mercury Compounds.

Isopropyl mercury compounds have not been made by any of the usual methods for making alkyl mercury compounds. The electrolytic reduction of acetone in sulfuric acid with a mercury cathode gives as a by-product a volatile mercury compound which is probably mercury di-isopropyl.[109]

Mercury Isobutyl Compounds.

Mercury Di-isobutyl.[110]

Preparation.

Five parts of isobutyl iodide and one part of pure ethyl acetate are shaken with twice the calculated amount of dilute sodium amalgam (1 : 400) in a large separatory funnel. The reaction takes place with the evolution of heat. After shaking about one hour heat is no longer evolved and water and ether are added to the mixture. The ether layer is separated and distilled on the water bath and then at a higher temperature. Steam distillation gives three layers, hydrocarbon, water, and mercury alkyl. No unchanged iodide is left. The products are di-isobutyl and the mercury compound. These are separated by fractional distillation under a pressure of 70 mm., the hydrocarbon boiling at 100° and the mercury alkyl at 140°.

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[109] Tafel, *Ber.* 39 (1906), 3626.

[110] Cahours, *Compt. rend.* 77 (1873), 1405. *J. prakt. Chem.* (2) 8 (1873), 397. Marquardt, *Ber.* 21 (1888), 2038.

Another method of preparation is to use 2 per cent sodium amalgam and add iodide and amalgam gradually. The mixture is treated with water and the insoluble liquid is fractionated, the mercury compound boiling at 205-7° under atmospheric pressure.

Properties.

Mercury di-isobutyl is a colorless liquid which is almost odorless cold but has a strong odor when hot. It is only very slightly soluble in water but soluble in alcohol and ether. B.P. 205-7°, at 70 mm. 140°. Its density at 15° is 1.835. It is volatile with steam.

Reactions.

1. With halogens.[111]

Iodine and bromine readily form isobutyl halides and the corresponding alkyl mercuric halides.

2. With metals.

Zinc and *aluminum* heated with the mercury dialkyl in sealed tubes at 130° give isobutyl compounds of the metals.

Isobutyl mercuric hydroxide.

The iodide reacts with moist silver oxide giving a strongly basic solution which reacts with acids giving salts of mercury di-isobutyl.

Isobutyl mercuric iodide.

Mercury di-isobutyl reacts with iodine forming this compound and isobutyl iodide. It is a crystalline solid.

Secondary-butyl Mercury Compounds.

Mercury Di-sec-butyl.[112]

This substance is prepared by electrolytic reduction of methyl ethyl ketone in sulfuric acid using a mercury cathode. The anode liquid is 20 per cent sulfuric acid while the cathode liquid is 30 per cent. The temperature is kept at 45° as lower temperatures give simple reduction as the chief process. A current of 25 amperes per square decimeter is passed at 7 or 8 volts. In one and a half hours 30 gm. of the ketone gives about 40 gm. of an oil which is separated, washed, dried with sodium sulfate, and vacuum distilled below 80°. The boil-

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[111] Cahours, loc. cit.

[112] Tafel, *Ber.* 39 (1906), 3628.

ing point at 0.3 mm. is 46°. Only about 30 per cent of pure product is obtained from the crude oil. An unstable yellow residue remains after the distillation. The mercury alkyl cannot be distilled at ordinary pressure. At 15 mm. it boils at 91-93° (CHHg).

An ether solution of mercury di-sec-butyl reacts with iodine forming sec-butyl iodide and a white crystalline compound which. is probably sec-butyl mercuric iodide as it reacts with more iodine giving the alkyl iodide.

Isoamyl Mercury Compounds.

Mercury di-isoamyl.[113]

Preparation.

Five parts of isoamyl iodide and one part of ethyl acetate are shaken with dilute sodium amalgam. A lively reaction ensues. It is necessary to cool the mixture from time to time. When heat is no longer evolved the ethyl acetate is distilled off on the steam bath. Steam is then passed through the mixture until about one-half of the oily residue has passed over. The residue is washed with water, dried with calcium chloride and analyzed.

Properties.

Mercury di-isoamyl is a colorless transparent mobile liquid of faint amyl odor. It cannot be distilled with an ordinary vacuum apparatus. If heated above 140° it decomposes. It is only slightly volatile with steam. It is insoluble in water, slightly soluble in alcohol, and readily soluble in ether. Sp. g. at 0° is 1.666. (CHHg).

Reactions.

1. With halogens.

When a little of the mercury alkyl is dropped into chlorine it gives white fumes of isoamyl mercuric chloride. Solid iodine dropped into the liquid reacts with a hissing sound. Bromine acts less violently. An ether solution reacts with iodine forming isoamyl iodide and isoamyl mercuric iodide.

2. With metals.

Sodium reacts forming sodium isoamyl. If the reaction is carried

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[113] Frankland and Duppa, *Ann.* 130 (1864), 110. *J. Chem. Soc.* 16 (1863), 420. Marquardt, *Ber.* 21 (1888), 2038. L. W. Jones, *J. Am. Chem. Soc.* 40 (1918), 1269. *Chem. Abst.* 12 (1918), 2820.

out in ether and carbon dioxide is passed through the mixture isobutyl acetic acid is formed.[114]

Zinc heated with the mercury compound for 36 hours in a sealed tube at 130° gives zinc di-isoamyl.[115]

3. With acids.[116]

Mercury di-isoamyl heated with glacial acetic acid at 190° for 16 hours gives isopentane, metallic mercury, and an amount of amyl acetate corresponding to one-quarter of the amyl originally present.

4. With mercuric salts.

The mercury compound treated with alcoholic mercuric chloride gives isoamyl mercuric chloride.

Isoamyl mercuric chloride.

The only preparation used is that just mentioned. It crystallizes in white hairlike needles from hot alcohol. It is insoluble in water but very soluble in hot alcohol and ether. M.P. 86°. It sublimes on gentle heating. The best method of purifying the substance is by dissolving it in hot alcohol and precipitating it by adding water. In this way the last traces of mercuric chloride are removed more completely than by simple recrystallization from alcohol. (Cl.)

Isoamyl mercuric iodide.

Very small amounts of this substance are obtained by the action of metallic mercury on isoamyl iodide in sunlight.[117]

The iodide has been prepared from the dialkyl compound and iodine in ether solution. The first crystals obtained are washed with dilute alcohol and dried between filter papers. Recrystallization from hot alcohol gives small pearly leaflets. If the alcohol used for recrystallization contains a few drops of alcoholic potassium hydroxide the crystallization is much delayed and the substance separates in large tablets. It is slightly soluble in boiling water. Cooling the hot aqueous solution gives fine crystals. It is readily soluble in ether. M.P. 122°. When heated to 140° the melted substance turns yellow and some mercuric iodide begins to separate. It can be sublimed in a stream of hot air. (CHIHg.)

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[114] Schorigin, *Ber.* 41 (1908), 2722; 43 (1910), 1937.

[115] Frankland and Duppa, loc. cit.

[116] L. W. Jones, loc. cit. 1269.

[117] Frankland and Duppa, loc. cit. Frankland, *Ann.* 85 (1853), 364.

n-Octyl Mercury Compounds.

Mercury Dioctyl.[118]

Preparation and properties.

n-Octyl iodide is treated with a very dilute sodium amalgam until no more heat is evolved. The mixture is extracted with ether and the ether is evaporated leaving an oil of very penetrating odor. This product cannot be distilled. At 200° it gives metallic mercury and dioctyl. Its density at 17° is 1.342. The product as obtained is nearly pure. (CHHg.) It is insoluble in water, easily soluble in alcohol, ether, and benzene.

Reactions.

1. With halogens.

It reacts with alcoholic iodine forming octyl mercuric iodide.

2. With mercuric salts. With alcoholic mercuric chloride it gives octyl mercuric chloride.

Octyl mercuric hydroxide.

The chloride in hot alcohol is treated with moist silver oxide. After standing for five hours the mixture is filtered hot. On cooling the filtrate deposits yellow leaflets. M.P. 75°. The product is a strong base. It is insoluble in cold water, slightly soluble in hot, and very easily soluble in alcohol. It liberates ammonia from ammonium salts and precipitates hydroxides from solutions of salts of iron, aluminum, zinc, and copper. (CHHg).

Octyl mercuric chloride.

The product from mercury dialkyl and mercuric chloride gives white crystals from alcohol. (ClHg).

Octyl mercuric iodide.

Alcoholic mercuric iodide and the mercury dialkyl give a silvery white precipitate which is easily soluble in hot alcohol. (IHg).

Mercury Compounds from Methylene Iodide.

Methylene iodide reacts with metallic mercury forming compounds containing one or two atoms of mercury depending on the amount of the metal used.

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[118] Eichler, *Ber.* 12 (1879), 1880.

Iodomethyl mercuric iodide, $I-CH_2-HgI$.[119]

Methylene iodide reacts with the calculated amount of mercury in sunlight forming the mono-mercury compound and a small amount of an extremely insoluble tri-mercurated compound which is due to an impurity of iodoform in the methylene iodide used. The reaction takes place more rapidly if the halide contains a trace of iodine or mercurous iodide. The mono-mercury compound is soluble only in hot methylene iodide. M.P. 109°. Refluxing with alcoholic mercuric chloride replaces the iodine attached to carbon by chlorine forming chloromethyl mercuric iodide, $Cl-CH_2-HgI$. Treatment with bases gives metallic mercury at once. Treatment with hydrochloric acid or with potassium iodide solution gives methyl mercuric iodide. No explanation of this unusual reaction is known.

Methylene di-mercuric iodide, $CH_2(HgI)_2$.

It is prepared like the preceding compound but by using an excess of mercury. Its properties are like those of the mono-mercury compound but it is even less soluble. Treatment with hydrochloric acid gives inorganic mercury and methyl mercuric iodide. The substance reacts with ethyl iodide but the products have not been identified.

Methine tri-mercuric iodide, $CH(HgI)_3$.

This substance is obtained as a by-product in the preparation of the above substances from methylene iodide containing a little iodoform. It is insoluble in all solvents, even hot methylene iodide. It reacts with iodine giving iodoform.

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[119] Sakurai, *J. Chem. Soc.* 37 (1880), 658; 39 (1881), 485; 41 (1882), 360.

Chapter V.

Mercury Compounds Obtained from the Olefines.

Mercury Compounds of Ethylene.[1]

Ethylene reacts with aqueous solutions of mercuric salts giving various complicated mercury compounds. From these have been obtained two types of simpler mercury compounds, ethanol mercuric salts and diethyl ether mercuric salts, $CH_2OH — CH_2 — HgX$ and $O(CH_2 — CH_2 — HgX)_2$ respectively. Substances believed to be vinyl mercury compounds of the formula $CH_2 = CH — HgX$ have since been found to be ethanol mercuric salts.

If the reaction between ethylene and mercuric salts is carried out in alcohol instead of in water it takes place more rapidly. The product corresponds to the ethanol mercuric salts but has an alkoxyl group instead of the hydroxyl of the latter compounds, $RO — CH_2 — CH_2 — HgX$.

The original workers with these substances expressed the opinion that there might be two forms of the ethanol mercuric salts, 1—that indicated, and 2—an intermediate addition product of a molecule of ethylene and a molecule of a basic mercuric salt, $C_2H_4.Hg(OH)X$. Later investigators go farther and claim that all of these ethylene mercury compounds are merely molecular addition compounds and do not correspond to any structural formulas.[2] The three types of products would then be represented by the formulas

"Ethanol mercuric salts," $C_2H_4.Hg(OH)X$
"Ethyl ether mercuric salts," $2C_2H_4.HgO.HgX_2$
Product from reaction in alcohol, ROH, $C_2H_4.Hg(OR)X$.

Neither the "structure" formulas nor the "addition" formulas are entirely satisfactory. The original conception of the compounds as true C — Hg compounds does not explain the fact that all three of

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[1] Hofmann and Sand, *Ber.* 33 (1900), 1340, 2692. Biilmann, *Ber.* 33 (1900), 1641. Sand, *Ber.* 34 (1901), 1385, 2906. Sand and Singer, *Ber.* 35 (1902), 3170. Sand and Breest, *Z. physik. Chem.* 59 (1907), 424.

[2] Manchot, *Ber.* 53 (1920), 984.

these substances react with dilute halogen acids giving quantitative yields of ethylene. The "addition" formulas explain the ready formation of ethylene by treatment with acids and alkyl halides but give no explanation of the fact that the compounds of this kind under proper conditions give ethyl alcohol, ethylene iodhydrine, and ββ′-di-iododiethyl ether.

Complex compounds obtained from ethylene and mercuric salts.

A compound, $C_6H_{10}O_4Cl_4Hg_4$, is obtained as a white precipitate by passing ethylene into an aqueous solution not quite saturated with mercuric chloride. It forms thin shining doubly refractive plates. On standing about twelve hours larger crystals separate which can easily be removed leaving the fine plates which are the desired substance. The larger crystals consist of a double salt of mercuric chloride and ethanol mercuric chloride. The fine crystals are almost insoluble in hot alcohol. (CHClHg). Warming with acid gives ethylene quantitatively. The compound, $HgCl_2.(CH_2OH - CH_2HgCl)$, consists of the larger crystals as just described. (CHClHg). It is soluble in a large amount of water. It can be recrystallized from methyl or ethyl alcohol. Bases precipitate only one-half of the mercury as the oxide. Hydrogen sulfide slowly precipitates all of the mercury as mercuric sulfide. The filtrate from the mercuric sulfide contains alcohol. This fact seems to favor the conception that the ethanol mercury compound is in reality a mercurated ethyl alcohol. Potassium cyanide or acids give ethylene with the mercury compound. The compound, $C_6H_{10}O_4Hg_4(SO_4)_2$, is precipitated by passing ethylene into an almost neutral mercuric sulfate solution. (CHSHg). When heated with acids it gives a quantitative yield of ethylene. This substance has been claimed to be ethanol mercuric sulfate $(CH_2OH - CH_2 - Hg)_2SO_4$ but the evidence appears to favor the more complex formula.

Ethanol mercuric chloride, $CH_2OH - CH_2 - HgCl$.

Mercuric nitrate solution is treated with potassium hydroxide solution until a slight precipitate of the basic salt persists after shaking. Ethylene is passed in to dissolve the precipitate. More alkali is added and then more ethylene. This is kept up until no more ethylene is absorbed. The filtered solution is then treated with the calculated amount of potassium chloride and allowed to stand for a few hours. Carbon dioxide is then passed in to precipitate the chloride from its alkaline solution. The mother liquor is evaported to dryness and extracted with methyl alcohol to recover the last of the chloride. It is recrystallized from methyl alcohol. (CHHg). M.P. 155°. Hydrochloric acid gives ethylene. The solubility of the chloride at 25° is about .01 mole per liter of water. The change in its conductivity with dilution indicates considerable hydrolysis.[3]

Ethanol mercuric bromide.

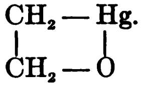
Its preparation is like that of the chloride just described. It also is recrystallized from methyl alcohol. (CHBrHg). It is soluble in 20.5 parts of alcohol at 22° and in 3.33 parts at 80°. It gives ethylene with 20 per cent hydrochloric acid at 15°. It reacts very slowly with 30 per cent acetic acid in the cold but gives ethylene rapidly on heating. Cold bases dissolve the bromide giving a clear solution. Ammonium sulfide gives a white precipitate.

An alkaline solution of sodium stannite gives mercury and a poisonous volatile mercury compound having a strong smell like carbylamine. This substance may be $Hg(CH_2 — CH_2OH)_2$.

An alcoholic solution of the bromide treated with bromine and potassium hydroxide gives a white crystalline substance which analyzes for a mercurated acetic acid, $BrHg — CH_2 — CO_2H$.

The bromide dissolved in absolute alcohol reacts with dry ammonia giving a white crystalline precipitate of $CH_2OH — CH_2HgBr.NH_3.(NH_3)$. M.P. 150°.

A solution of the bromide in the least possible amount of boiling alcohol deposits fine crystals on cooling. When the cold mixture is treated with sodium ethylate solution the crystals dissolve. After a few minutes a thick white powder separates. This is washed with hot absolute alcohol. M.P. 146°, not sharp. It is soluble in cold water giving an alkaline solution. Small amounts of dilute acids give white precipitates which dissolve in an excess of acid forming ethylene. This substance may be the anhydride of β-hydroxymercuri-ethyl alcohol,



Ethanol mercuric iodide.

Its preparation is like that of the chloride and bromide. (Hg). M.P. 147°. Hydrochloric acid gives ethylene. Reduction in alkaline solu-

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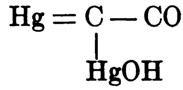
[3] Sand and Breest, *Z. physik. Chem.* 59 (1907), 424.

tion by electrolysis or by sodium amalgam gives ethyl alcohol which is identified by transforming it to iodoform and to silver acetate.[4] It is easily soluble in one molecule of alkali. It also dissolves in alcoholic sodium ethylate. When this solution is treated with methyl iodide and refluxed the original iodide is recovered unchanged. The iodide reacts with iodine giving ethylene iodhydrine. Heating the iodide with methyl iodide gives mercuric iodide, ethylene, and methyl alcohol. Heating with mercuric oxide and potassium hydroxide gives mercurihydroxymercuri-acetic acid,  $\underset{\displaystyle HgOH}{Hg = \overset{}{C} — CO_2H}$.[5]

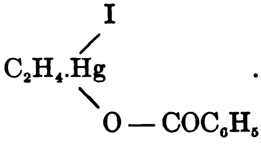
Ethanol mercuric nitrate.

It is prepared from the chloride and silver nitrate in methyl alcohol. The filtrate is evaporated over sulfuric acid. (NHg). When heated it decomposes with a slight puff and the formation of red vapors. Hydrochloric acid precipitates the chloride. An excess of acid must be avoided as it liberates ethylene. Potassium cyanide solution also gives ethylene. Oxygen acids give this reaction only very slightly.

Ethanol mercuric sulfide. $(CH_2OH — CH_2 — Hg —)_2S$.

An alkaline solution of the chloride is treated with potassium sulfide. A pure white precipitate is obtained (CHSHg). Boiling the sulfide with water gives a solution which on cooling deposits crystals of *ethanol mercuric sulfhydrate* which can be recrystallized from water. (CHSHg).

Benzoate of ethanol mercuric iodide, $C_6H_5CO—O—CH_2—CH_2—HgI$.[6]

A solution of the iodide in 10 per cent potassium hydroxide is treated with benzoyl chloride. The white precipitate obtained is purified by dissolving in alcohol and precipitating by water and potassium iodide solution. It can be recrystallized from alcohol. (CHHg). M.P. 118°. It is easily soluble in organic solvents but is insoluble in water and in alkalies. Fuming hydrochloric acid gives ethylene slowly. This inactivity may be due to the extreme insolubility of the substance in water. Manchot formulates this substance as  $C_2H_4.Hg\begin{matrix} / I \\ \backslash O — COC_6H_5 \end{matrix}$.

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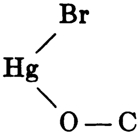
[4] Sand and Singer, *Ber.* 35 (1902), 3180.

[5] Hofmann and Sand, *Ber.* 34 (1901), 1385, 2906.

[6] Sand, *Ber.* 34 (1901), 1390. Manchot, *Ber.* 53 (1920), 984.

Treatment of ethanol mercuric bromide with acetic anhydride does not give an acetyl derivative. The compound obtained is described as a "mono-mercury acetic acid" and has the formula $C_2H_3O_2BrHg$. (CHHg). However, its sharp melting point of 117-18° marks it as being different from the known bromomercuri acetic acid. It may be a "mixed" salt of mercury,



$$Hg\begin{cases} Br \\ O-COCH_3 \end{cases}.$$

ββ′-Di-chloromercuri diethyl ether, $O(CH_2-CH_2-HgCl)_2$.[7]

A practically neutral solution of mercuric sulfate is obtained by dissolving yellow mercuric oxide in 30 per cent sulfuric acid, adding more of the oxide until some insoluble basic salt is formed, and then filtering the solution. The solution is treated with ethylene. A white precipitate forms almost at once. After about 8 hours the precipitate is filtered, washed, and treated with 15 per cent potassium hydroxide which dissolves all but a slight black residue. The filtered alkaline solution is treated with potassium chloride and saturated with carbon dioxide. The chloride separates as a white crystalline precipitate. It is difficultly soluble in water, alcohol, and ether. M.P. 190°, not sharp. (CHClHg).

The chloride can also be obtained from the complex precipitate formed from ethylene and mercuric chloride. It does not react as readily with acids as does the corresponding ethanol mercury compound. It does however form ethylene slowly. This slowness of reaction may be due to its slight solubility in aqueous reagents.

The corresponding *bromide* is made in the same way as the chloride. It forms a fine white powder which is almost insoluble in water, alcohol, and ether. At 24° it dissolves in 6595 parts of absolute alcohol. It sinters about 200° (CHHg). It reacts slowly with acids giving ethylene. It dissolves in sodium hydroxide giving a clear solution.

The *iodide* is prepared in the same way as the other halides except that it precipitates from the cold alkaline solution without the use of carbon dioxide. It is purified by recrystallization from 15 per cent potassium hydroxide. M.P. 161°. Treatment of the iodide with iodine in potassium iodide gives a 90 per cent yield of ββ′-di-iododiethyl ether. This is obtained by steam distillation as a colorless oil. (CHI). Its structure is proved by converting it to morpholine,

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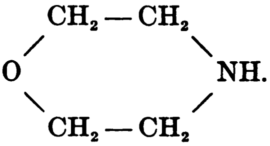
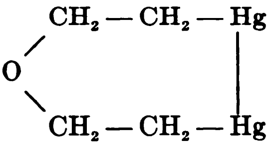
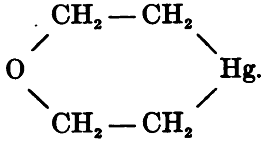
[7] Sand, *Ber.* 34 (1901), 2907.



This is done by heating the di-iodide with toluene sulfonamide and decomposing the resulting compound with hydrochloric acid at 170°. The morpholine hydrochloride obtained melts 175-6°. It is further identified by changing it to the picrate and the chloroplatinate. The di-iododiethyl ether also gives a monoquinoline salt melting at 176° (CHI), and a diquinoline salt melting with decomposition at 254° (I).

The corresponding *carbonate* $O(CH_2 — CH_2 — Hg —)_2CO_3$, is obtained by passing carbon dioxide directly into the alkaline solution of the product obtained from ethylene and mercuric sulfate. It is a white solid soluble in alkalies. (CH,CO_3,Hg).

Cyclic mercury compounds obtained from the diethyl ether di-mercuric halides.[8]

Treatment of the halides with an alkaline sodium stannite solution gives a gray violet precipitate of an organic mercur*ous* compound,  , which is fairly stable as it requires a temperature of 140° to change it to metallic mercury and the corresponding mercur*ic* compound, 

Mercurous diethylene oxide, $O = (CH_2 — CH_2)_2 = Hg_2$.

It is prepared as just mentioned by adding a filtered sodium stannite solution to an alkaline solution of diethyl ether di-mercuric bromide or the original precipitate from ethylene and the barely acid solution of mercuric sulfate. The product forms as a gray violet precipitate in almost quantitative yield. It sinters about 80° and melts 140-150°. (CHHg). When dry it forms a gray black powder insoluble in water, alkalies, and organic solvents. Heated in a tube with dry

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[8] Sand, *Ber.* 34 (1901), 2913.

ether or benzene for a few hours at 140° it gives mercury and crystals of the mercuric compound.

Mercuric diethylene oxide, $O = (CH_2 - CH_2)_2 = Hg$.

It is prepared from the mercurous compound as just described. It forms long thin colorless prisms from benzene. Yield 60 per cent. M.P. 145°. (CHHg). It has a peculiar odor. It is insoluble in water, alkalies, and dilute mineral acids, but easily soluble in warm benzene, toluene and alcohol. It is difficultly soluble in ether and very difficultly soluble in acetone. Potassium hydroxide, potassium iodide, and potassium cyanide give no action even on long boiling. This stability to potassium cyanide is in sharp contrast to the easy formation of ethylene from the ethanol mercury compounds. However, fuming hydrochloric acid gives ethylene and mercuric chloride.

A benzene solution reacts with an ether solution of picric acid giving a crystalline picrate. (CHN). Its formation is probably due to the oxygen in the six membered ring.

A cold benzene solution reacts with an ether solution of mercuric chloride forming a precipitate containing two molecules of mercuric chloride. (CH). This substance is formulated as an addition product, $O = (CH_2 - CH_2)_2 = Hg.2HgCl_2$. It may be that one molecule of the mercuric chloride acts as mercuric salts always do with $C - Hg - C$ compounds forming ββ'-di-chloromercuri diethyl ether. The other molecule of mercuric chloride would then be more loosely combined.[9] In fact sodium hydroxide is said to precipitate "some" of the mercury in the compound as the oxide. A quantitative determination of the fraction of the mercury precipitated in this way would decide which of these explanations is correct.

Products Obtained from Ethylene and Mercuric Salts in Alcohol.[10]

Ethylene is absorbed much more rapidly by a solution of mercuric acetate in methyl alcohol than by an aqueous solution. The product is formed by the addition of the groups $-HgOAc$ and $-OCH_3$ to the ethylene double bond. When other alcohols are used the corresponding alkoxyl group appears in the product. If the product is not regarded as a "structural" compound it may be formulated as

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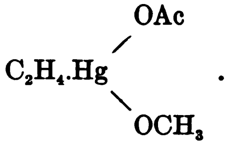
[9] Stoehr, *J. prakt. Chem.* (2) 55 (1897), 80.

[10] Schoeller and Schrauth, *Ber.* 46 (1913), 2867. Manchot, *Ber.* 53 (1920), 986.



$$C_2H_4.Hg\begin{matrix}\diagup OAc\\ \diagdown OCH_3\end{matrix}\ .$$

α-Acetoxymercuri-β-methoxy ethane, $AcOHg — CH_2 — CH_2 — OCH_3$.

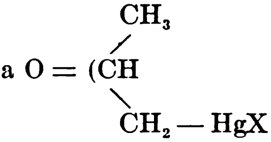
Ethylene free from air is passed into mercuric acetate in methyl alcohol in a special shaking apparatus. In one hour almost exactly one mole of ethylene is absorbed and all of the acetate is dissolved. Most of the alcohol and the acetic acid formed in the reaction are removed by distillation under diminished pressure. The oily residue solidifies on standing. It is recrystallized from low boiling ligroin. Yield 82 per cent. M.P. 42°. (CHHg). It is very soluble in water and common solvents. It gives bad blisters on the skin. A water solution treated with a little hydrochloric acid gives a precipitate of the corresponding chloride. An excess of acid gives ethylene on warming. Alkalies and carbonates give no visible change. Ammonium sulfide in the cold gives a white amorphous precipitate which blackens slowly in the cold but rapidly on heating. Sodium stannite solution gives metallic mercury even in the cold. At first a slight violet color appears. This may indicate the formation of an unstable mercurous compound. No product except the mercury is mentioned. The acetate decolorizes permanganate and iodine solutions.

The corresponding *bromide* is obtained from an alcoholic solution of the acetate and an aqueous solution of potassium bromide. It forms white leaflets from dilute alcohol. The solution of the substance in ethyl acetate can be precipitated by low boiling ligroin. M.P. 58° (CHBrHg). It is very readily soluble in organic solvents except low boiling ligroin (petroleum ether). It is rather difficultly soluble in cold water. The *iodide* is obtained in the same way as the bromide. It is purified by dissolving in ethyl acetate and precipitating with low boiling ligroin. Its solubilities resemble those of the bromide. It is not very stable. (CHIHg).

α-Acetoxymercuri-β-ethoxy ethane.

It is prepared in the same way as the methoxy compound. Yield 95 per cent. It is very soluble in water and organic solvents including low boiling ligroin. (CHHg,MW). On rapid heating it sinters at 33° and melts at 36°. The *chloride* is prepared from the acetate and sodium chloride. It is purified from ethyl acetate and low boiling ligroin. (CHClHg). M.P. 92°. It is very soluble in alcohol, chloroform, ethyl acetate, and acetone, fairly soluble in ether and benzene, less soluble in water and very difficultly soluble in ligroin, both low and high boiling. When the chloride is heated with methyl iodide at 100° mercuric salts and almost exactly one mole of ethylene are produced. The *bromide* and *iodide* are prepared in the same way but have not been studied in detail.

Mercury Compounds Obtained from Propylene.[11]

Propylene reacts with mercury salts giving two types of compounds corresponding to those obtained from ethylene, propanol mercuric salts of the formula $CH_3-CHOH-CH_2HgX$, and isopropyl ether mercuric salts of the formula  $O=\left(CH\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_2-HgX\end{smallmatrix}\right)_2$. In the addition to the double bond the mercury adds to the carbon having the most hydrogen atoms.

a-Acetoxymercuri-β-hydroxypropane, $CH_3-CHOH-CH_2-HgOAc$.

A solution of the substance is obtained from propylene and mercuric acetate solution. The pure substance has not been isolated. Treatment with potassium permanganate solution does not give the mercurated acetone which might be expected but a more complex product $C_6H_{12}O_5Hg_3$ which has not been further studied. (CHHg).

The corresponding *chloride* is made by treating basic mercuric nitrate with propylene and adding the calculated amount of potassium chloride. The preparation is carried out in the same way as with ethylene. The chloride is so soluble that it cannot be precipitated from the alkaline solution by carbon dioxide but has to be extracted with ether. It is recrystallized from ether. (CHHg). M.P. about 53°. The *bromide* is prepared in the same way as the chloride. After the addition of the potassium bromide to the alkaline solution the mixture is allowed to stand for 12 hours and is then saturated with carbon dioxide. The precipitate is crystallized from a mixture of absolute

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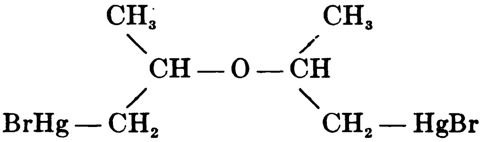
[11] Hofmann and Sand, *Ber.* 33 (1900), 1354. Sand and Singer, *Ber.* 35 (1902), 3172. Sand and Genssler, *Ber.* 36 (1903), 3704.

alcohol and ether. (CH). M.P. 76°. The bromide cannot be oxidized to the corresponding mercurated acetone but gives the complex mercury compound obtained from the chloride. The *iodide* is prepared in the same way as the bromide. It is recrystallized from benzene forming fine needles. (CH,I high,Hg). M.P. 68°. It is easily soluble in absolute alcohol and ether, difficultly soluble in carbon disulfide, benzene and water. It reacts with hydrochloric acid giving propylene.

Reduction of the iodide with sodium amalgam followed by acidification with sulfuric acid, treatment with silver nitrate, filtration, oxidation by potassium dichromate and sulfuric acid, distillation with alkali, and treatment with hydroxylamine gives acetone oxime melting at 60°. This shows that the original substance was a substituted isopropyl alcohol.

Alkaline solutions of the propanol mercuric halides react with hydrogen sulfide forming a white precipitate which is soluble in excess of sulfide. The two substances are probably the sulfide and the hydrosulfide of the organomercuric residue.

Di-bromomercuri di-isopropyl ether,



.[12]

It is obtained as a small insoluble residue during the preparation of the propanol compound. It is purified by dissolving in pure potassium hydroxide and precipitating by carbon dioxide. It is a heavy crystalline powder insoluble in all common solvents. (CHHg). It does not melt. The corresponding *iodide* is obtained from an alkaline solution of the bromide and potassium iodide. It can be recrystallized from hot alkali. It is insoluble in all common solvents. (Hg).

Mercury Compounds from Isobutylene.[13]

A number of complex mercury compounds are obtainable from isobutylene. One which is obtained by means of mercuric nitrate is explosive on percussion or on warming to 80°. It is formulated as

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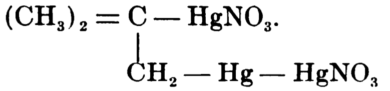
[12] Sand and Genssler, *Ber.* 36 (1903), 3704.

[13] Denigès, *Ann. chim. phys.* (7) 18 (1899), 386. Hofmann and Sand, *Ber.* 33 (1900), 1356.



$$\begin{array}{l}(CH_3)_2 = C - HgNO_3.\\ \quad\ | \\ \quad CH_2 - Hg - HgNO_3\end{array}$$

$(CHNHg,C_4H_8)$. Hydrochloric acid regenerates isobutylene and forms a mixture of mercuric and mercurous chlorides.

Chloromercuri hydroxy isobutane, $(CH_3)_2 = C(OH) - CH_2HgCl$.

A solution of the acetate or nitrate of mercury is treated with pure alkali until a slight permanent precipitate forms. The solution of the basic salt is then treated with isobutylene and alkali alternately until no more butylene reacts. The alkaline solution is treated with the calculated amount of potassium chloride and allowed to stand for 12 hours. It is then saturated with carbon dioxide and extracted with ether as the chloride does not precipitate out. The ether is evaporated. The residue is recrystallized from dry ether. (CH). M.P. 52°. The *bromide* is obtained in the same way but forms a precipitate when carbon dioxide is passed through its alkaline solution. The precipitate is extracted with ether and the product is recrystallized from benzene. (CHBrHg). Small shining prisms. M.P. 66°. Hydrochloric acid gives isobutylene. It is easily soluble in bases. Hydrogen sulfide gives a white oily precipitate which is easily soluble in an excess of hydrogen sulfide water and in alcohol. The bromide dissolved in dry ether reacts with ammonia forming a compound $C_4H_8(OH)HgBr.NH_3$. (CHg,NH_3). The substance obtained in the same way as the chloride and bromide but with the use of potassium iodide is probably the corresponding *iodide* although it appears in the literature as C_4H_7HgI.[14] It can be crystallized from dry ether, benzene, or carbon disulfide.

Mercury Compounds from the Higher Ethylene Hydrocarbons.

Trimethyl ethylene (amylene), sym. dimethyl ethylene, and dimethyl ethyl ethylene have been treated with mercuric salts. In some cases complex mercury compounds are obtained and in others the mercury salts act merely as oxidizing agents.[15]

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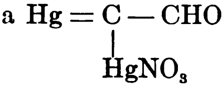
[14] Hofmann and Sand, *Ber.* 33 (1900), 1358.

[15] Hofmann and Sand, *Ber.* 33 (1900), 1340. Denigès, *Ann. chim. phys.* (7) 18 (1899), 385. *Bull. soc. chim.* (3) 19 (1898), 494. Balbiano and Paolini, *Ber.* 35 (1902), 2994. Balbiano, *Gazz. chim. ital.* 36 I (1906), 238.

Mercury Compounds from Acetylenes.

Acetylene reacts with solutions of mercuric salts giving extremely insoluble amorphous precipitates. When these precipitates are treated with mineral acids acetaldehyde is produced. This reaction first discovered by Kutscheroff[16] has become very important as a means of producing ethyl alcohol and acetic acid from acetylene. The nature of the organic mercury compounds first formed is by no means settled although many chemists have proposed formulas for them.[17] The problem is of theoretical rather than immediate practical interest as the mercurated products are not isolated but are continuously changed to acetaldehyde by the acid present during their formation. The rôle of the mercury salts thus becomes that of catalysts. Among the formulas which have been suggested for the intermediate mercury compounds obtained from acetylene and mercuric chloride are $Cl - CH = CH - HgCl$ and $(ClHg)_3C - CHO$. Monochloroacetylene reacts with mercuric chloride giving a product which is believed to be trichloromercuri-acetic acid.[18] Acetylene reacting with a slightly acid solution of mercuric nitrate gives a substance believed to have the formula



$$Hg = \underset{\substack{| \\ HgNO_3}}{C} - CHO.$$ [19]

Other investigators interpret these products from acetylene as "double compounds" of acetylene or mercury acetylide with various amounts of mercuric salts, mercuric or mercurous oxide, and water. Complicated formulas are arrived at which agree with the analytical results. The chief difficulty in the study of these compounds is their extreme insolubility which prevents their purification. Moreover the composition of the precipitates obtained undoubtedly varies considerably with changing conditions.

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[16] *Ber.* 14 (1881), 1540.

[17] Kutscheroff, loc. cit. Plimpton, *Proc. Chem. Soc.* 8 (1892) 110. Keiser, *Am. Chem. J.* 15 (1893), 537. Plimpton and Travers, *J. Chem. Soc.* 65 (1894), 266. Hofmann, *Ber.* 31 (1898), 2213, 2783. Köthner, *Ibid.* 2475. Erdmann and Köthner, *Z. anorg. Chem.* 18 (1898), 53. Biginelli, *Chem. Zentr.* 1898 I 925. Hofmann, *Ber.* 32 (1899), 874. LeComte, *J. pharm. chim.* (6) 16 (1902), 297. *Chem. Zentr.* 1902 II 1499. Burkard and Travers, *J. Chem. Soc.* 81 (1902), 1270. Biltz and Mumm, *Ber.* 37 (1904), 4417. Hofmann, *Ibid.* 4459. Biltz, *Ber.* 38 (1905), 133. Brame, *J. Chem. Soc.* 87 (1905), 427. Nieuwland and Maguire, *J. Am. Chem. Soc.* 28 (1906), 1025. Biltz and Reinkober, *Ann.* 404 (1914), 219. Manchot, *Ann.* 417 (1918), 93. Patents, *Chem. Abst.* 11 (1917), 870, 2027; 12 (1918), 42, 280, 484, 566, 588.

[18] Hofmann and Kirmreuther, *Ber.* 42 (1909), 4237.

[19] Hofmann, *Ber.* 31 (1898), 2213.

The hydration of acetylene to form acetaldehyde does not necessarily mean that the intermediate mercury compounds have an aldehyde structure. The hydration of the triple bond may merely be catalyzed by the mercuric ions in acid solution. Cases are known in which this hydration takes place under the influence of dilute acid alone. Such a case is that of piperonyl acetylene which gives the corresponding ketone on warming with dilute hydrochloric acid.[20]

The *monohalogenated acetylenes* react with alkaline mercuric cyanide solution in an atmosphere of hydrogen forming compounds of the type $Hg(C \equiv CX)_2$.[21]

Mercury bis-monochloroacetylene, $Hg(C \equiv CCl)_2$.

Monochloroacetylene is shaken with an alkaline solution of mercuric cyanide in an atmosphere of hydrogen to prevent the explosion which would result from a mixture of the monosubstituted acetylene and air. A white precipitate is formed. This is dried and extracted with much warm ether. Evaporation of the solution gives rectangular doubly refractive plates. (CClHg). M.P. 185°. If the heating is continued an explosion takes place which is less violent than that of mercury acetylide. The solid reacts with potassium cyanide giving pure monochloroacetylene. The corresponding *bromine compound* is prepared in the same way and has similar properties.

Methyl acetylene (*allylene*) reacts with mercuric salts giving precipitates which react with acids giving acetone. The intermediate compounds are formulated as tri-mercurated acetones or as double compounds of mercuric salts with mercury methyl acetylide. Allylene reacts with mercuric oxide and water giving *mercury methyl acetylide,* $Hg(C \equiv C - CH_3)_2$. (CHHg).[22]

Ethyl acetylene gives compounds much like those of methyl acetylene. Treatment with acids gives methyl ethyl ketone. The true nature of the mercury compounds is not settled although they may well be tri-mercurated compounds of the type

$$CH_3 - CH_2 - CO - C(HgX)_3.$$

Isopropyl acetylene reacts with mercuric bromide giving a product which acts with acids giving methyl isopropyl ketone.[23]

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[20] Manchot and Haas, *Ann.* 399 (1913), 150.

[21] Hofmann and Kirmreuther, *Ber.* 41 (1908), 316; 42 (1909), 4236.

[22] Kutscheroff, *Ber.* 17 (1884), 13. Biltz and Mumm, *Ber.* 37 (1904), 4426.

[23] Perkin, *Chem. Abst.* 7 (1913), 2095.

Methyl n-butyl acetylene reacts with mercuric chloride.[24]

Ethyl propyl acetylene gives a white precipitate with mercuric chloride which reacts with hydrochloric acid giving an odor of butyrone.[25]

Mercury Compounds of Cyclopentadiene and Dicyclopentadiene.

Di-chloromercuri cyclopentadiene.[26]

Cyclopentadiene reacts with mercuric chloride in alcoholic solution giving a white crystalline precipitate insoluble in all solvents. (CHCl,Hg low). The white precipitate decomposes in contact with alcohol even with the exclusion of air and light. It is believed to be a polymer because of its insolubility. This property may simply be due to the presence of two mercury atoms on the methylene carbon. No evidence has been secured as to the structure of the compound.

Chloromercuri methoxy di-cyclopentadiene.[27]

Dicyclopentadiene does not react with mercuric chloride in ether solution. If the reaction is carried out in alcohol solution crystalline soluble products are obtainable. These are formed by the addition of a chloromercuri group and an alkoxyl group to one of the double bonds of the dicyclopentadiene. The other double bond cannot be made to enter the reaction.

Dicyclopentadiene is treated with mercuric chloride in acetone free methyl alcohol. The solution is allowed to stand at room temperature for two days and is then heated to boiling and diluted with water until a slight turbidity forms. On standing fine crystals separate. The product is obtained as slightly yellowish needles from 60 per cent methyl alcohol. (CHClHg). Yield 10 gm. from 5 gm. of the hydrocarbon. M.P. 133°. It is easily soluble in methyl and ethyl alcohols, ether, acetone, benzene, gasoline, and acetic acid. Acids regenerate dicyclopentadiene which gives the characteristic compound with sulfurous acid. Boiling potassium cyanide solution has the same effect as acids. It is soluble in hot alkalies. Careful addition of acid to the alkaline solution reprecipitates the chloride. There is no evidence as to the positions taken by the added groups. The corresponding *ethoxy* compound is

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[24] Béhal, *Bull. soc. chim.* (2) 49 (1888), 582.

[25] Béhal, *Ann. chim. phys.* (6) 15 (1888), 415.

[26] Thiele, *Ber.* 34 (1901), 71. Hofmann and Seiler, *Ber.* 39 (1906), 3187.

[27] Hofmann and Seiler, loc. cit.

prepared by the action of mercuric chloride in ethyl alcohol on dicyclopentadiene. Its properties are like those of the methoxy compound. (CHClHg). It forms colorless doubly refractive prisms. M.P. 98°. The substance is stable in a vacuum at 80° showing that it contains an ethoxy group rather than alcohol of crystallization. The molecular weight found by the freezing point method in benzene is 392, calculated 412.5. The *amyloxy* compound can be prepared in isoamyl alcohol. It is a heavy oil which solidifies at —12° (C high, HClHg low).

Mercury Compounds from Unsaturated Halides.

Vinyl bromide reacts with solid mercuric acetate when heated at 100° for a few hours forming an amorphous white precipitate and acetaldehyde. The precipitate is believed to be a compound of acetaldehyde with one molecule of mercurous bromide. Heated to 100° it gives acetaldehyde.[28]

The mercury compounds obtained from the *monohalogen acetylenes* and an alkaline mercuric cyanide solution have already been described under acetylene.

Mercury bis-trichlorethylene, $Hg(CCl = CCl_2)_2$.[29]

Trichlorethylene is shaken with an alkaline solution of mercuric cyanide for several days. The oily layer is separated and the excess of trichlorethylene is distilled off under diminished pressure. The residue is recrystallized from ether or chloroform. It forms colorless shining plates. (CClHg). M.P. 83°. Chlorine acts with the compound only in strong light and then gives perchlorethane and mercuric chloride. The corresponding *bromine compound* is prepared from alkaline mercuric cyanide and acetylene tetrabromide. Tribromethylene is first formed by the alkali and then reacts giving the mercury compound. Crystalline leaflets of $Hg(CN)_2.KBr.H_2O$ separate. An odor of dibromacetylidine is also noted. After ten hours the solid is extracted with water, dried, and extracted with warm ether. After the ether is evaporated the product is dissolved in hot alcohol and precipitated by water. The product crystallizes from ether in colorless doubly refractive prisms. (CBrHg). M.P. 141°. It is soluble in alcohol and

[28] Saytzeff and Glinsky, *Z. Chem.* (2) 3 (1867), 675. Kutscheroff, *Ber.* 14 (1881), 1540.

[29] Hofmann and Kirmreuther, *Ber.* 41 (1908), 314; 42 (1909), 4234.

ether. Ammonium polysulfide gives mercuric sulfide and tribromethylene. Hot 10 per cent hydrochloric acid hardly attacks it. Even hot concentrated potassium cyanide solution acts only very slowly forming tribromethylene.

Allyl mercuric iodide, $CH_2 = CH — CH_2 — HgI$.[30]

Allyl iodide and an equal volume of alcohol are shaken with metallic mercury. The mercury quickly reacts forming a yellow crystalline mass. A trace of iodine or mercurous iodide hastens the reaction. Yield 90 per cent. The product crystallizes from alcohol in silvery flakes which turn yellow on standing. (CHIHg). It is soluble in hot alcohol, carbon disulfide, acetone, almost insoluble in cold alcohol, and insoluble in water. 100 parts of carbon disulfide at 49° dissolve 18.7 parts of the iodide leaving a dark yellow residue of $HgI_2.3HgO$. It has a garlic-like odor. It starts subliming at 100° forming rhombic plates. M.P. 135°. Heating above the melting point causes decomposition giving a gas, carbon, and a yellow sublimate. On standing it changes in some way to a substance having a larger per cent of mercury.

Allyl mercuric iodide reacts vigorously with an excess of *cold* potassium cyanide forming mercury, potassium iodide, mercuric cyanide, and diallyl. 500 gm. of allyl mercuric iodide gives 30 gm. of diallyl and 140 gm. of mercury as compared with the theoretical amounts of 53 gm. and 133 gm. respectively. A small amount of an explosive liquid is obtained. This reaction is without parallel among organomercuric iodides. Potassium cyanide usually gives no reaction unless heated with the dry iodide when it gives a poor yield of the mercury dialkyl.

When the iodide is treated with ether and an excess of zinc diethyl in the cold a vigorous reaction ensues forming a little gas, metallic mercury, zinc iodide, diallyl, and mercury diethyl.

In marked contrast to the ease with which allyl mercuric iodide reacts with potassium cyanide and zinc diethyl is the fact that it gives no reaction when heated with phosphorus tribromide, acetyl chloride, or benzoyl chloride.

Dry distillation of allyl mercuric iodide gives metallic mercury, mercuric iodide, and diallyl. This is the best method for making that substance.

[30] Zinin, *Ann.* 96 (1855), 363. Linnemann, *Ann. Spl.* 3 (1865), 262. *Ann.* 140 (1866), 180. Oppenheim, *Ber.* 4 (1871), 670.

A paste of the iodide with alcohol reacts with the calculated amount of iodine to form allyl iodide which can be distilled from the mixture. This process is used in the separation of allyl iodide and isopropyl iodide which is based on the fact that the latter substance does not react readily with metallic mercury.

A solution of the iodide in dilute nitric acid reacts readily with hydrogen sulfide giving propylene and mercuric sulfide. Hydriodic acid gives a similar splitting of the C — Hg linkage.

Allyl mercuric iodide heated with allyl iodide "probably" gives diallyl and mercuric iodide.[31] If the reaction takes place in the way indicated it represents another peculiar reaction of the iodide as organic mercury compounds do not usually react with organic halides to form longer carbon chains. In this case it would be impossible to follow the course of the reaction as allyl mercuric iodide itself gives diallyl on heating. The mercury formed could react with the allyl iodide present forming more allyl mercuric iodide which would produce more diallyl.

The iodide reacts with alcoholic silver nitrate giving a solution of *allyl mercuric nitrate.* In a similar way moist silver oxide gives an alcoholic solution of the *hydroxide* which is obtained as a syrup on evaporation. This is volatile on heating and has an odor of garlic. It reacts with acids forming salts.

Propargyl mercuric iodide, $CH \equiv C — CH_2 — HgI$.[32]

Propargyl iodide unites readily with metallic mercury. The product has not been studied in detail.

Mercury Derivatives of Aliphatic Nitro Compounds.[33]

The mercury derivatives of the nitro compounds were originally believed to be C — Hg compounds in much the same way that the sodium derivatives were believed to have the sodium attached to carbon. In all probability they are O — Hg compounds. Mercury bisnitroform is possibly an exception. In some solvents it gives a colorless solution which is a non-conductor. Such solvents are ether, ben-

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[31] Linnemann, loc. cit.

[32] Henry, *Ber.* 17 (1884), 1132.

[33] V. Meyer, *Ber.* 5 (1872), 516. Meyer and Rilliet, *ibid.* 1030. Meyer, *Ann.* 171 (1874), 31. Nef, *Ann.* 280 (1894), 270. L. W. Jones, *Am. Chem. J.* 20 (1898), 33. Ley and Kissel, *Ber.* 32 (1899), 1357. Ley, *Ber.* 38 (1905), 974. Scholl and Nyberg, *Ber.* 39 (1906), 1958. Prager, *Monatsh.* 33 (1912), 1289.

zene and its homologs, ethyl acetate, ethyl oxalate, chloroform, carbon tetrachloride, and lactic acid. It gives colored ionized solutions in water and pyridine. It has been suggested that the colorless form is a C — Hg compound and the colored an O — Hg compound.[34]

$Hg[C(NO_2)_3]_2$	$[(O_2N)_2C = N — O —]_2Hg$
Colorless	Colored
Non-ionized.	Ionized.

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[34] **Ley and Kissel, loc. cit. Ley, loc. cit.**

Chapter VI.

Mercury Compounds from Saturated and Unsaturated Alcohols.

Ethyl alcohol reacts with mercuric salts and with mercuric salts in the presence of alkalies giving a variety of ill defined compounds.[1] The only compounds of settled constitution are the mercarbides.

Alcohols cause a splitting of mercuric salts of oxygen acids analogous to hydrolysis. This alcoholysis appears to be more rapid with isopropyl and isobutyl alcohols than with the normal compounds.[2]

Tertiary alcohols heated with an acid solution of mercuric sulfate give a yellow precipitate containing mercury. On further heating mercurous sulfate is formed. This reaction has been recommended as a test for tertiary alcohols.[3]

Mercarbides.

Mercarbides are compounds having all of the hydrogen of a methyl group replaced by mercury.[4]

Ethane hexamercarbide, $C_2Hg_6O_2(OH)_2$.

Yellow mercuric oxide, potassium hydroxide, and ordinary alcohol are heated together under a reflux condenser for 36 hours. The grayish yellow residue is washed with water and dilute alkali and then with 20 per cent warm nitric acid to dissolve any mercury or tri-mercurated acetic acid present. The residue is the dinitrate of the mercarbide, $C_2Hg_6O_2(NO_3)_2$. It is pure white. The mercarbide itself is obtained

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[1] Sobrero and Selmi, *Ann.* 80 (1851), 108. *Jahresb.* (1815), 506. Gerhardt, *Ann.* 80 (1851), 111. Reynoso, *Ann. chim. phys.* (3) 48 (1856), 403. Cowper, *J. Chem. Soc.* 39 (1881), 242. Dimroth, *Ber.* 31 (1898), 2156. Marsh and Struthers, *J. Chem. Soc.* 95 (1909), 1778.

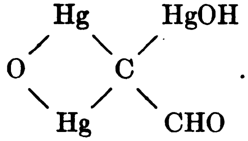
[2] Schoeller, Schrauth, and Struensee, *Ber.* 44 (1911), 1052 ff.

[3] Denigès, *Ann chim. phys.* (7) 18 (1899), 393. *Bull. soc. chim.* (3) 19 (1898), 751.

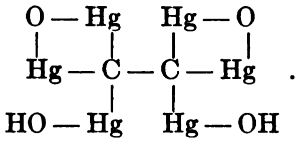
[4] Hofmann, *Ber.* 31 (1898), 1904, 2213; 32 (1899), 870; 33 (1900), 1328. Hofmann and Sand, *Ber.* 33 (1900), 1358. Hofmann and Feigel, *Ber.* 38 (1905), 3654. Hofmann and Wagner, *Ber.* 41 (1908), 1628.

by treating the nitrate with pure sodium hydroxide. The presence of any chloride will change part of the mercury base into the chloride. The base is slightly yellow. (CHHg). Yield, 57 gm. of the mercarbide from 100 gm. of mercuric oxide. About 40 per cent of the mercuric oxide used is reduced to metallic mercury. About 2 per cent of tri-mercuri-acetic acid is obtained. Considerable amounts of aldehyde resin and oxalic acid are also formed.

The probable course of the reaction is as follows: the alcohol is first oxidized by one molecule of mercuric oxide to acetaldehyde which is then mercurated by three molecules of mercuric oxide giving the anhydride of tri-hydroxymercuri acetaldehyde,



This is oxidized by another molecule of the oxide to the sodium salt of the corresponding tri-mercuri acetic acid. Two molecules of this substance lose sodium oxalate leaving the mercarbide,



$$\begin{array}{ccccccc} \text{O} & - & \text{Hg} & & \text{Hg} & - & \text{O} \\ | & & | & & | & & | \\ \text{Hg} & - & \text{C} & - & \text{C} & - & \text{Hg} \\ & & | & & | & & \\ \text{HO} & - & \text{Hg} & & \text{Hg} & - & \text{OH} \end{array} .$$

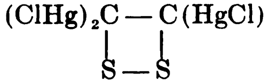
This mechanism would call for a yield of 60 gm. of mercarbide from 100 gm. of oxide whereas 57 gm. are obtained.

The mercarbide can also be obtained from acetaldehyde, propyl alcohol, allyl alcohol, amyl alcohol, cellulose, and starch. Methyl alcohol and formaldehyde give none of it.

The mercarbide base is a yellowish white very insoluble powder. It reacts with acids forming salts which are very stable to an excess of acid, hydrogen sulfide, potassium cyanide, and even aqua regia. It is also stable to powerful oxidizers such as potassium permanganate, chromic acid, hypochlorites and hypobromites. It reacts very slowly with reducing agents such as sulfurous acid, hydroxylamine, and hydrazine. When heated it explodes at about 230° with extreme brisance. It is, however, stable to concussion.

Treatment of the mercarbide with acids gives two sets of salts, one in which the two hydroxyl groups have been replaced by acid radicals and the other in which all of the oxygen groups have been replaced giving salts of the type $C_2Hg_6X_6$. Hydrogen sulfide reacts with the mercarbide giving a complex sulfide but no mercuric sulfide. The extraordinary stability of the $C-Hg$ linkages in this substance can be shown by the fact that treatment of this sulfide with chlorine water, nitric acid, and sodium hydroxide gives the original hexamercarbide. (CHHg).

A methyl alcohol solution of ammonium polysulfide acts slowly on the mercarbide. If the mixture is allowed to stand for several weeks with frequent renewals of the polysulfide solution the mercarbide is finally changed to a deep yellow powder. If this is treated with hydrogen sulfide it turns black. Treatment with potassium sulfide restores the yellow color. The yellow substance is very insoluble. It has the formula $C_2Hg_6O_2S_2H_2$. (CHSHg). It has two atoms of sulfur in place of two atoms of oxygen in the original mercarbide.

The mercarbide reacts with a 10 per cent solution of sulfur monochloride in benzene forming mercuric chloride and an intensely yellow crystalline compound,  $\begin{array}{c}(ClHg)_2C-C(HgCl)_2\\ |\qquad|\\ S-S\end{array}$. (CClSHg). This is insoluble in all solvents. It is stable to boiling concentrated hydrochloric acid. When heated with sodium hydroxide it gives a dark yellow product which does not explode on heating.

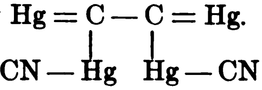
Long boiling with hydrazine hydrate gives a mixture of nitrogen and a combustible gas which is probably ethane.

When the mercarbide is heated it turns dark red before it explodes. This change of color may be due to the loss of another molecule of water leaving a compound $C_2Hg_6O_3$ which is the real explosive substance. The products of the explosion contain mercury, carbon dioxide, and other substances.

The mercarbide reacts with an excess of sodium bisulfite solution giving a light yellow substance which turns gray in light. If the yellow substance is treated with nitric acid and then boiled with pure sodium hydroxide the original mercarbide is recovered.

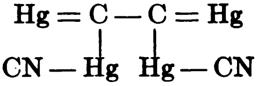
The mercarbide forms a picrate which is less explosive than potassium picrate.

Long boiling of the mercarbide with potassium cyanide solution gives an intensely yellow solid of lower specific gravity than the original substance. Its formula is $C_2Hg_4(CN)_2$. (CNHg). Its structure is probably



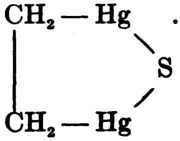
$\mathrm{Hg}=\underset{\mathrm{CN—Hg}}{\underset{|}{\mathrm{C}}}—\underset{\mathrm{Hg—CN}}{\underset{|}{\mathrm{C}}}=\mathrm{Hg}$. It explodes slightly on heating.

It is soluble in cold 15 per cent nitric acid. Treatment of this solution with hydrogen sulfide gives a white precipitate of a compound, $C_2Hg_4S_2H_2$, which is probably the sulfhydrate corresponding to the cyanide used. (CHSHg). The cyanide reacts with hydrochloric acid forming hydrocyanic acid and a compound, $C_2Hg_4Cl_4H_2$, which probably has the structure of a tetra-mercurated ethane, $(ClHg)_2CH—CH(HgCl)_2$. If this substance is heated with concentrated hydrochloric acid it gives a crystalline volatile compound having the formula $ClHg—CH_2—CH_2—HgCl$. (CHClHg). This substance separates in the condenser and receiver in colorless rectangular leaflets. It has an intense odor somewhat resembling that of hydrocyanic acid. It is volatile even at room temperature. It is easily soluble in water, alcohol, and ether. M.P. 173°. It is rather poisonous. A solution in hydrochloric acid acts with potassium iodide giving white needle crystals which are not attacked by dilute acids but dissolve in bases. This iodide can be recrystallized from alcohol and ether in quadratic plates. When the tetramercarbide dicyanide,



$\mathrm{Hg}=\underset{\mathrm{CN—Hg}}{\underset{|}{\mathrm{C}}}—\underset{\mathrm{Hg—CN}}{\underset{|}{\mathrm{C}}}=\mathrm{Hg}$,

is treated with an aqueous solution of potassium polysulfide it is changed to a yellow precipitate, $C_4Hg_4SH_6$. (CHSHg). This may be an organic sulfide, $(Hg=CH—CH_2—Hg—)_2S$. If ammonium polysulfide in methyl alcohol is used instead of the aqueous potassium polysulfide the product is a yellow substance having the formula, $C_2Hg_2SH_4$. (CHSHg). This is probably

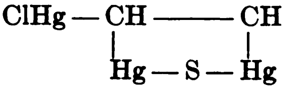


Ethane hexamercarbide dichloride, $C_2Hg_6O_2Cl_2$.

This substance is prepared from the mercarbide and a hot chloride solution or cold 10 per cent hydrochloric acid. (Cl). It reacts with ammonia giving a yellow white compound, $C_2Hg_6O_2(NH_3)_2Cl_2$. (NClHg).

The corresponding *nitrate, sulfate,* and *perchlorate* have been prepared and analyzed.

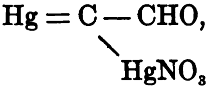
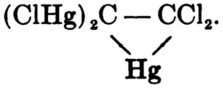
Ethane hexamercarbide hexachloride, $(\mathrm{ClHg})_3\mathrm{C-C}(\mathrm{HgCl})_3$.

Ethane hexamercarbide is heated with 10 per cent hydrochloric acid. The product is a white insoluble substance. (CClHg). It decomposes quietly on heating. Boiling with sodium hydroxide gives the original base. When treated with a water solution of potassium polysulfide in the dark it gives yellow crystals of a compound,  $\begin{array}{ccccc} \mathrm{ClHg-} & \mathrm{CH} & \text{——} & \mathrm{CH} & \mathrm{-HgCl} \\ & | & & | & \\ & \mathrm{Hg} & \mathrm{-S-} & \mathrm{Hg} & \end{array}$. (CHClSHg). Boiling hydrochloric acid gives an odor like that of the di-chloromercuri ethane mentioned above. A white crystalline product is obtained at the same time. This reacts with sodium hydroxide to form a yellow non-explosive compound. Treatment of the hexachloride with sulfur monochloride dissolved in benzene or undiluted gives no action.

The corresponding hexa-iodide, $C_2Hg_6I_6$, is obtained on heating ethane hexamercarbide with ethyl iodide and ether for 60 hours at 90°. (CIHg).

The remarkable reactions noted in the study of ethane hexamercarbide are summarized in the chart on page 130.

Mercarbides from Acetylene.[5]

Acetylene passed into a cold mercuric nitrate solution gives a precipitate which may have the structure,  $\begin{array}{l} \mathrm{Hg=C-CHO} \\ \qquad\ \diagdown \\ \qquad\quad \mathrm{HgNO_3} \end{array}$, (Hg). Acetylene passed into a solution of mercuric chloride and sodium chloride gives a precipitate which may be  $\begin{array}{c} (\mathrm{ClHg})_2\mathrm{C-CCl_2} \\ \diagdown\ \diagup \\ \mathrm{Hg} \end{array}$. (C,Cl low,Hg low). Long washing with water lowers the chlorine content still more. Boiling dilute hydrochloric acid gives considerable acetaldehyde.

Mercarbides from Acetic Acid.[6]

Sodium acetate refluxed with mercuric chloride in absolute alcohol for 20 hours gives a white crystalline powder which is purified by extraction with 15 per cent warm nitric acid and then with 30 per cent cold nitric acid. (CClHg). The same product can be obtained from

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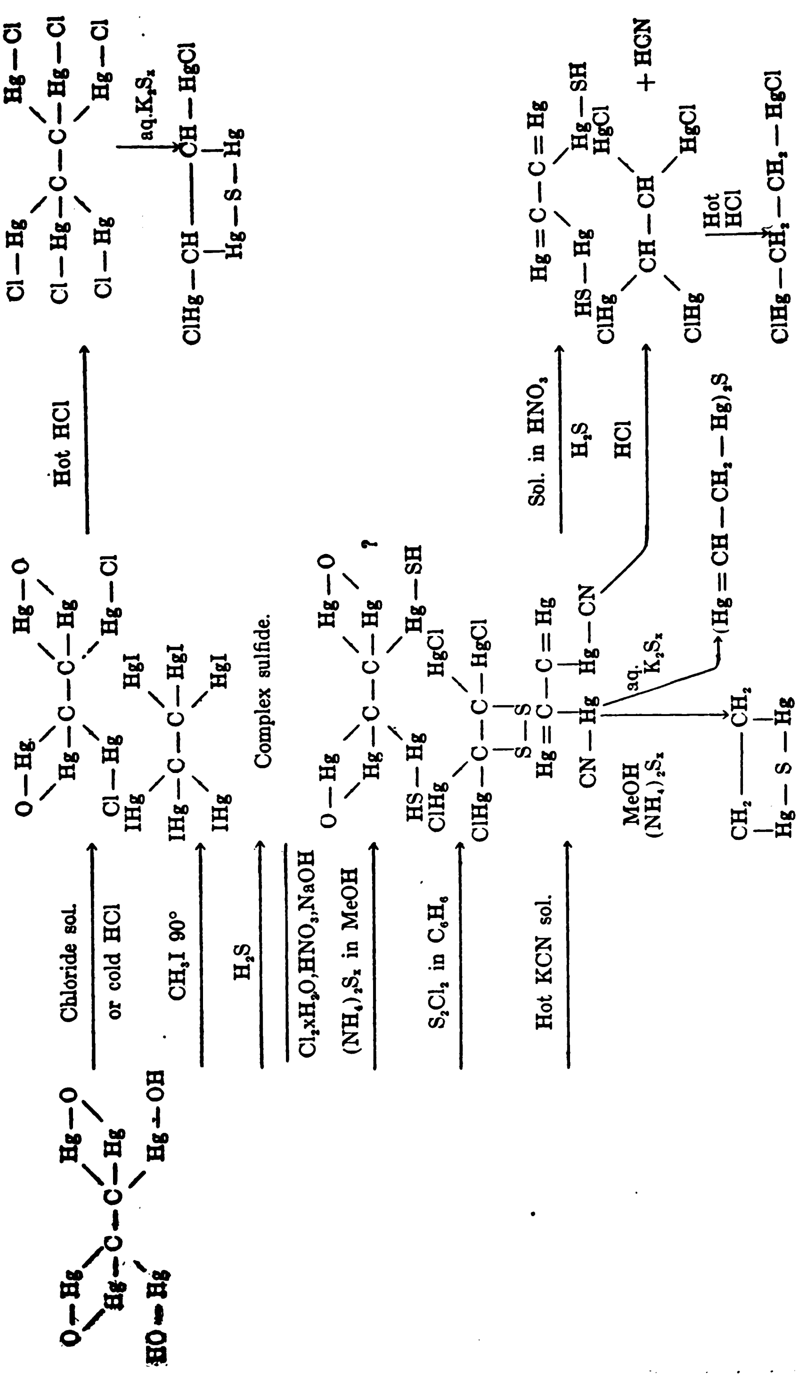
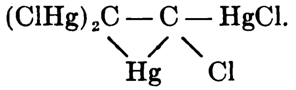
[5] Hofmann, *Ber.* 31 (1898), 2213, 2783; 32 (1899), 870.

[6] Hofmann, *Ber.* 32 (1899), 870.


Chloride sol.
or cold HCl
CH3I 90°
H2S
Complex sulfide.
Cl2,xH2O,HNO3,NaOH
(NH4)2Sx in MeOH
S2Cl2 in C6H6
Hot KCN sol.
Hot HCl
aq.K2Sx
Sol. in HNO3
H2S
HCl
+HCN
Hot HCl
aq. K2Sx
MeOH (NH4)2Sx
(Hg=CH—CH2—Hg)2S
?

sodium propionate or sodium butyrate. The white substance is blackened by bases and by potassium cyanide. It might indeed be mistaken for mercurous chloride but for the fact that it is partly soluble in hot sodium hydroxide. The treatment with bases or cyanides gives an odor of acetaldehyde. The solution obtained by means of hot sodium hydroxide contains tri-mercuri-acetic acid and some of the corresponding di-mercuri compound. The original substance probably has the structure



$$\begin{array}{l}(\mathrm{ClHg})_2\mathrm{C}-\mathrm{C}-\mathrm{HgCl}.\\ \qquad\;\diagdown\;\diagup\;\diagdown\\ \qquad\quad\mathrm{Hg}\quad\mathrm{Cl}\end{array}$$

Other Mercarbides.

Potato starch gives a mercarbide, $C_3Hg_2O_2H_6(NO_3)$.[7]
Acetone gives $C_3Hg_3O_3H_5$.[8]
Cane sugar gives $C_3Hg_4O_6H_6(NO_3)$.[9]

Mercury Compounds of Unsaturated Alcohols.

Vinyl Alcohol.[10]

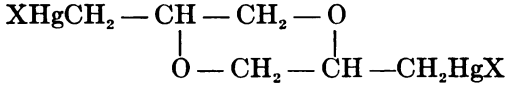
Crude diethyl ether shaken with mercury oxychloride, $HgO.HgCl_2$, gives a precipitate to which is assigned the formula

$$\text{“}CH_2 = CHOHgOHgCl_2\text{”}.$$

(CHClHg). It is blackened by bases. It dissolves in acetic acid giving a crystalline acetate.

Allyl Alcohol.[11]

Considerable work has been done on the action of mercuric salts on allyl alcohol and the products obtained have been formulated in a variety of ways. The problem like all those involving the action of mercuric salts with unsaturated compounds cannot be regarded as settled. It seems probable that only two classes of compounds are obtained, the propylene glycol mercuric salts of the type $CH_2OH - CHOH - CH_2HgX$, and the dipropylene oxide di-mercuric salts of the type



$$\begin{array}{l}\mathrm{XHgCH_2-CH-CH_2-O}\\ \qquad\qquad\quad|\qquad\qquad\;|\\ \qquad\qquad\;\mathrm{O-CH_2-CH-CH_2HgX}\end{array}$$

. The lat-

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[7] Hofmann, *Ber.* 33 (1900), 1333.

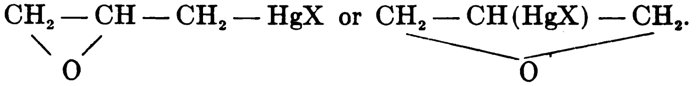
[8] Hofmann, *Ber.* 31 (1898), 1908.

[9] Hofmann, *Ber.* 33 (1900), 1333.

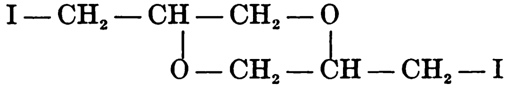
[10] Poleck and Thümmel, *Arch. Pharm.* Nov. 1889. *Ber.* 22 (1889), 1866.

[11] Hofmann and Sand, *Ber.* 33 (1900), 1358. Biilmann, *ibid.* 1641. Hofmann and Sand, *ibid.* 2692. Sand, *Ber.* 34 (1901), 1385, 2906. Biilmann, *Ber.* 35 (1902), 2586, Sand and Singer, *ibid.* 3170.

ter compounds have been incorrectly formulated as allene mercuric compounds, $CH_2=C=CH-HgX$; as allyl alcohol mercuric compounds, $CH_2OH-CH=CH-HgX$; and as propylene oxide mercuric compounds,



The propylene glycol mercuric salts are made by treating basic mercuric nitrate with allyl alcohol and precipitating the alkaline solution with potassium iodide, etc. The dipropylene oxide di-mercuric salts are obtained by allowing allyl alcohol to react on an acid solution of mercuric nitrate forming crystals of the organic mercuric nitrate which can be dissolved in alkali and precipitated by potassium halides. The formation of the two types of products is explained by assuming that the first stage in the reaction is the addition of $-X$ and $-HgX$ to the double bond forming an unstable product, $CH_2OH-CHX-CH_2HgX$. In the presence of alkali the acid group on the middle carbon is hydrolyzed off giving a propylene glycol mercuric salt. In acid solution this does not take place but two molecules react with the elimination of two molecules of HX forming a dipropylene oxide compound containing a six membered ring having the same structure as di-epi-iodhydrine which probably has the structure



.[12]

The difference in the two types of compounds obtained from allyl alcohol are well shown by a comparison of the properties of the two bromides.[13]

Propylene glycol compound.	Di-propylene oxide compound.
$C_3H_7O_2-HgBr$.	$(C_3H_5O-HgBr)_2$.
M.P. 84-6°.	M.P. 251°.
Easily soluble in alcohol and acetone.	Insoluble in organic solvents.
Easily decomposed by HCl.	Not changed by HCl.
Alkaline solution gives no action with KI.	KI forms a white precipitate.
Ditto + KCN gives no action.	KCN forms a white precipitate.
Ditto + H_2S gives no action.	H_2S forms a white precipitate.

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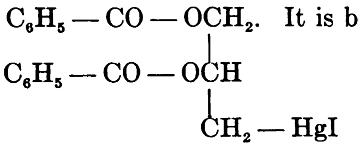
[12] Stoehr, *J. prakt. Chem.* (2) 55 (1897), 88.

[13] Hofmann and Sand, *Ber.* 33 (1900), 2700.

Proylene glycol mercuric iodide, $CH_2OH-CHOH-CH_2-HgI$.[14]

Yellow mercuric oxide is dissolved in 20 per cent nitric acid and the solution is treated with pure dilute potassium hydroxide until a slight permanent precipitate of the basic nitrate is formed. Allyl alcohol is added and the mixture is shaken until the precipitate dissolves. More base is added to form a precipitate and the precipitate is dissolved in more allyl alcohol. The alternate addition of base and allyl alcohol is continued until the addition of base gives a black precipitate. The alkaline solution is filtered, treated with potassium iodide solution, allowed to stand 24 hours, and saturated with carbon dioxide. A yellow viscous oil separates which, when dried, forms a crystalline mass containing some drops of mercury. This is crystallized from benzene or dry ether in which it is difficultly soluble. A better method of purification is by dissolving it in alcohol or acetone, decolorizing the solution with bone black, adding one-fifth volume of benzene, and evaporating in vacuo. The substance forms white plates melting at 80°. (CHHg). Hydrochloric acid or even acetic acid after a few minutes standing gives mercuric salts and allyl alcohol.

A solution of the iodide in 10 per cent potassium hydroxide reacts on shaking with benzoyl chloride giving a *dibenzoyl derivative,*

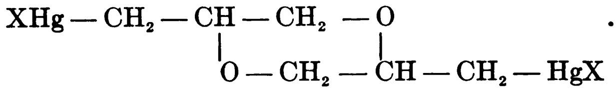


$$\begin{array}{l} C_6H_5-CO-OCH_2 \\ \qquad\qquad\qquad\quad | \\ C_6H_5-CO-OCH \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad CH_2-HgI \end{array}$$

It is best purified by dissolving in alcohol and pouring into potassium iodide solution. M.P. 100°. (CH). It is stable to fuming hydrochloric acid.

The corresponding *bromide* is prepared the same as the iodide. It is purified by dissolving in acetone, adding benzene, and concentrating in a vacuum. White crystals. (CHBrHg). On rapid heating it melts 84-6°. At 110° it decomposes with evolution of gas. It is more soluble in water than the iodide. It is easily soluble in alcohol and acetone. It is rapidly decomposed by hydrochloric acid.

Di-mercuri Compounds of Di-propylene oxide.



$$\begin{array}{l} XHg-CH_2-CH-CH_2-O \\ \qquad\qquad\qquad\quad | \qquad\qquad\quad | \\ \qquad\qquad\qquad\quad O-CH_2-CH-CH_2-HgX \end{array}$$

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[14] Hofmann and Sand, *Ber.* 33 (1900), 2698.

The *nitrate* has probably never been obtained in a pure state. If a fairly strongly acid solution of mercuric nitrate is treated with allyl alcohol an exothermic reaction takes place. The solution must be cooled to 0° to avoid the formation of extremely insoluble products. After several days a large amount of a crystalline substance separates. It is soluble in alkalies and ammonium hydroxide. Ammonium sulfide and hydrogen sulfide gives white precipitates. It reacts with halides and cyanides to form the corresponding organomercuric salts. The solution in ammonium hydroxide deposits fine white crystals of a compound containing ammonia. The nitrate may also be obtained by treating allyl alcohol with mercur*ous* nitrate. In this case metallic mercury is formed.

The *sulfate* is obtained from allyl alcohol and an acid solution of mercuric sulfate.[15] The reaction mixture must be kept cooled to 20°. It is soluble in water and in base solutions. It can be purified by crystallization from water containing a little allyl alcohol. It then contains $4H_2O$. ($CHHg,SO_4,H_2O$). It forms a compound with two molecules of ammonia. (SO_4,NH_3). When treated with bromine it gives the corresponding bromide if an excess of the halogen is avoided.

The *chloride* is prepared by treating an alkaline solution of the nitrate with dilute hydrochloric acid or potassium chloride and carbon dioxide. (CHHg). Another preparation is from a complex double compound of mercuric chloride formed from mercuric chloride solution and allyl alcohol.[16] This compound is treated with 10 per cent alkali which converts one-third of the mercury in the compound into mercuric oxide. The filtrate when saturated with carbon dioxide gives a precipitate of the chloride. (CHCl low, Hg). The chloride reacts with zinc and dilute hydrochloric acid giving an odor of allyl alcohol. Boiling with 20 per cent hydrochloric acid gives mercuric chloride and a variety of compounds including allyl chloride, allyl ether, propylene glycol, methyl ethyl acrolein, and propionaldehyde. Potassium permanganate oxidizes the chloride giving oxalic acid among other products.

The *bromide* is prepared in the same way as the chloride. It is almost insoluble in organic solvents. (CHBr). M.P. 251°. Its molecular weight by the boiling point method in ethylene dibromide is found to be 605 as compared with the calculated value of 674.

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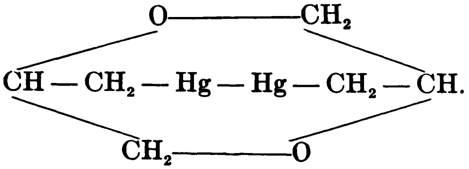
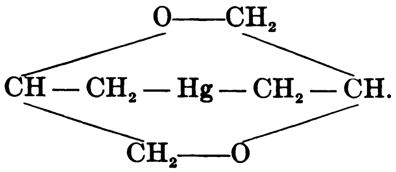
[15] Biilmann, *Ber.* 33 (1900), 1642.

[16] Hofmann and Sand, *Ber.* 33 (1900), 1359.

An alkaline solution of the bromide reacts with sodium stannite giving a brick red precipitate of an organic mercur*ous* compound,

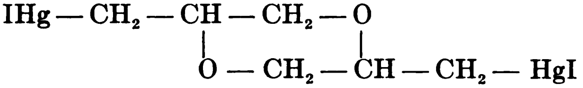


(CHHg low). Standing in sunlight changes this red substance to a gray powder from which hot benzene extracts a substance which appears in colorless crystals when the benzene solution is treated with acetone and cooled. This substance is the corresponding murcur*ic* compound,



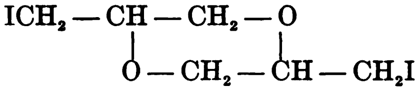
Poor yield. (CHHg). M.P. about 190°. It is insoluble in water, potassium hydroxide, dilute acids, easily soluble in benzene and toluene, and insoluble in acetone. It is not changed by boiling with potassium hydroxide, iodide, or cyanide. A benzene solution gives a precipitate with mercuric chloride dissolved in ether. This may well be the dichloromercuri di-propylene oxide.

The *iodide*,



$$\begin{array}{ccccccccccccc} \mathrm{IHg} & - & \mathrm{CH_2} & - & \mathrm{CH} & - & \mathrm{CH_2} & - & \mathrm{O} & & & & \\ & & & & | & & & & | & & & & \\ & & & & \mathrm{O} & - & \mathrm{CH_2} & - & \mathrm{CH} & - & \mathrm{CH_2} & - & \mathrm{HgI} \end{array}$$

, is prepared from an alkaline solution of the nitrate and potassium iodide solution. In this case no carbon dioxide is needed to cause precipitation as the iodide differs from the chloride and bromide in not being soluble in cold alkalies. The iodide can be recrystallized from boiling alkali. (CHIHg). M.P. 271°. It is practically insoluble in the common organic solvents but can be recrystallized from boiling benzyl chloride. This is a good example of the failure of organic mercury compounds to react with organic halides. The iodide is not changed by 20 per cent hydrochloric acid. The hot alkaline solution gives a precipitate with potassium cyanide. The iodide reacts but slowly with iodine in potassium iodide solution. It reacts with iodine in benzene in a tube at 140° giving di-epi-iodohydrine which probably has the structure,



$$\begin{array}{l}\mathrm{ICH_2-CH-CH_2-O}\\ \qquad\qquad\ \ |\qquad\qquad\quad |\\ \qquad\qquad\ \mathrm{O-CH_2-CH-CH_2I}\end{array}$$

.[17]

The *cyanide* is prepared from the alkaline solution of the nitrate by adding potassium cyanide. It forms a thick white precipitate which is insoluble in alkali even on heating. (CHNHg).

The *hydroxide* is prepared from the chloride and moist silver oxide. The water solution is alkaline and precipitates the hydroxides of heavy metals from their solutions. The same hydroxide is probably obtained by allowing allyl alcohol and water to react on freshly prepared yellow mercuric oxide. The alkaline solution so prepared reacts with hydrobromic acid forming di-bromomercuri di-propylene oxide. (Br).

The *acetate* is obtained from allyl alcohol and an acid solution of mercuric acetate. It forms a white crystalline precipitate. When dried over calcium chloride it retains half a molecule of water. (CHHg). When recrystallized from hot water it is obtained anhydrous. (CHHg). It gives precipitates with potassium bromide and with dilute hydrochloric acid. It dissolves in alkalies and in ammonium hydroxide. Ammonium sulfide gives a white precipitate. Boiling in water does not decompose the acetate.

A *basic carbonate* is obtained by passing carbon dioxide into an alkaline solution of the nitrate. The precipitate contains one molecule of the carbonate for three of the hydroxide. ($CHHg,CO_2$).

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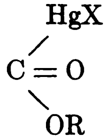
[17] Stoehr, *J. prakt. Chem.* (2) 55 (1897), 88.

Chapter VII.

Mercury Derivatives of Fatty Acids.

Mercury Compounds from Carbon Monoxide.[1]

Mercuric salts in alcohol add to carbon monoxide in much the same way that they add to ethylene compounds. As in the case of all such reactions the products may be formulated as true structure compounds or as molecular addition compounds,  $\mathrm{C}(\mathrm{HgX})(=\mathrm{O})\mathrm{OR}$ or $CO.Hg(OR)X$.

Neither formula explains all of the reactions. Acids and alkyl halides liberate carbon monoxide, a fact which throws doubt on the first formula. Various reactions give formic acid derivatives, a fact which is hard to explain by the second formula.

Acetoxymercuriformic methyl ester, $AcOHg — CO_2CH_3$.

A methyl alcohol solution of mercuric acetate is treated with carbon monoxide under two atmospheres pressure in a specially constructed shaking apparatus. The gas is absorbed slowly for about 24 hours. Almost exactly one mole is absorbed. Small amounts of mercurous acetate and carbon dioxide are formed. The reaction mixture is filtered and the filtrate is evaporated under diminished pressure at about 35°. An oil is left which solidifies on standing. The solid is dissolved in chloroform by gentle warming and then treated with five volumes of 40-60° ligroin. Crystals soon separate. (CHHg). Yield 88 per cent. Correcting for the mercurous acetate formed the yield is 95 per cent. On rapid heating it melts 109° (corr. 110°) with decomposition. It is easily soluble in methyl and ethyl alcohols, chloroform, fairly soluble in warm water, ethylacetate, acetone, and benzene, diffi-

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[1] Schoeller and Schrauth, *Ber.* 46 (1913), 2869. Manchot, *Ber.* 53 (1920), 984.

cultly soluble in ether and low and high boiling ligroin. Heating gives carbon monoxide, mercurous acetate and other products which have not been identified. Its molecular weight by the boiling point method in chloroform is 310 as compared with the calculated value of 318. A freshly prepared sample of the acetate is completely soluble in ammonium hydroxide without the formation of any black product. Ammonium sulfide does not give mercuric sulfide until the mixture has stood for a few minutes. The other product is carbon monoxide.

.1 normal halogen acids precipitate the corresponding halogen mercuri compound. 5. normal halogen acid gives carbon monoxide immediately. Concentrated sulfuric acid evolves almost exactly one mole of carbon monoxide. Cold dilute nitric acid and acetic acid give only a slow decomposition. Hot dilute nitric acid liberates carbon dioxide instead of the monoxide. Normal sodium hydroxide dissolves the acetate giving a clear solution from which mercury soon separates leaving a solution of sodium bicarbonate. When the mercurated ester is heated with methyl iodide at 100° it gives mercuric iodide, mercuric acetate, and almost exactly one mole of carbon monoxide.

Acetoxymercuriformic ethyl ester.

It is prepared in the same way as the methyl ester. In ethyl alcohol solution the absorption of the carbon monoxide takes three times as long as in methyl alcohol. Needle crystals are obtained. (CHHg). It sinters and starts to decompose at 65°. At 125° it decomposes very rapidly. It is easily soluble in alcohol, chloroform, acetone, and ethyl acetate, fairly soluble in warm water, ether, benzene, less soluble in cold water, and hardly at all in ligroin.

The ester can be changed to ethyl formate by treatment with two equivalents of aluminum activated by mercuric chloride. A water solution is used. The reaction takes about two hours. During this time the mixture must be kept cold or some carbon monoxide will be liberated. This peculiar formation of carbon monoxide would favor the conception of the compound as a loose molecular addition product. When the reaction is complete the mixture is warmed to 50° and hydrogen is blown through it. The escaping vapors are passed through tubes cooled in a Dewar cylinder containing solid carbon dioxide and ether. An 80 per cent yield of pure ethyl formate boiling at 54.5° is obtained. The calculated amount of metallic mercury is formed.

Chloromercuriformic methyl ester.

The acetate dissolved in methyl alcohol is treated with a solution of sodium chloride. Long white needles are formed. (CHClHg). Yield 80 per cent. On rapid heating it sinters and decomposes at 109° but gives no melting point. It is easily soluble in acetone, ethyl acetate, chloroform, and alcohol, fairly soluble in warm water, benzene, and ether, less soluble in cold water, and very little soluble in ligroin.

When the chloride is suspended in ether it decolorizes iodine and goes into solution. Some mercuric iodide separates. A strong odor of a halogen formic ester is noticeable. The solution is cooled and ammonia is passed in. Ammonium chloride is filtered off, the filtrate is treated with hydrogen sulfide to remove all mercury, and the mixture is again filtered. Evaporation of the filtrate leaves an oily residue which solidifies on cooling and can be recrystallized from low boiling ligroin. It is proved to be methyl urethane by its melting point of 52° and analyses for C, H, and N. Yield 68 per cent.

Chloromercuriformic ethyl ester.

It is prepared in the same way as the methyl compound. It is recrystallized from warm water and alcohol. (CHClHg). It melts with decomposition at 87° (88° corr.). It is soluble in ethyl acetate, acetone, chloroform, less easily in water, ether, very difficultly in low boiling ligroin. Treatment with iodine in ether and then with ammonia gives a 70 per cent yield of ethyl urethane melting at 50° (N).

When the chloride is heated with n-propyl iodide at 100° a large amount of carbon monoxide is formed. No ethyl butyrate is obtained. This result is not surprising as organic mercury compounds do not react with alkyl iodides to give a lengthened carbon chain.

Bromomercuriformic methyl ester.

It is prepared from the acetate in the usual way. It is best recrystallized from ether. (CHBrHg). It decomposes 127-8° with evolution of gas. With hydrochloric acid it gives carbon monoxide. The corresponding *ethyl* compound is similarly prepared.

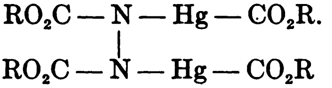
Iodomercuriformic methyl ester.

It is prepared like the chloride. It can be crystallized from ether in leafy crystals which are very unstable. (CHIHg). The crystals turn yellow on standing and finally decompose entirely giving mercurous iodide. The *ethyl* compound has been prepared.

Sulfide-mercuriformic methyl ester, $(CH_3O_2C-Hg-)_2S$.

A cold saturated methyl alcohol solution of the acetate is treated at 0° with slightly less than the calculated amount of a titrated solution of hydrogen sulfide. Any excess causes decomposition with evolution of carbon monoxide. The product is a white cheesy precipitate. (CHSHg). It is insoluble in all solvents. It is unstable, readily giving mercuric sulfide.

Other compounds have been made which may be regarded as mercurated formic esters.[2] They are obtained by the oxidation of hydrazine carboxylic esters with mercuric oxide and have the general formula,



$$\begin{array}{l} RO_2C-N-Hg-CO_2R \\ \qquad\quad\;\; | \\ RO_2C-N-Hg-CO_2R \end{array}$$

Bromine in benzene solution forms mercuric bromide, azodicarboxylic ester, $RO_2C-N=N-CO_2R$, and bromoformic ester which is identified by changing it to the corresponding urethane. Treatment with piperidine gives metallic mercury, hydrazodicarboxylic ester, $RO_2C-NH-NH-CO_2R$, and "piperylurethane," $C_5H_{10}=N-CO_2R$. The most interesting reaction of these substances is that with hydrochloric acid which gives a quantitative yield of carbon monoxide. The other products are alcohol, mercuric chloride, and hydrazodicarboxylic ester. This reaction shows that the grouping $-Hg-CO_2R$ is peculiar in its reaction with acids.

The *ethyl ester,* $(C_2H_5O_2C)_2N_2(Hg-CO_2C_2H_5)_2$, is prepared by treating the ethyl ester of hydrazine monocarboxylic acid with a suspension of freshly prepared pure mercuric oxide. A considerable amount of gas is evolved. This consists of nitrogen with traces of carbon monoxide and a compound which is probably an organic azide. The solid residue contains mercury and the product. The latter is extracted with boiling water. Yield 5 gm. of the mercury compound from 30 grams of the original ester. It is recrystallized from a small amount of hot benzene or toluene. M.P. 155°. (CHNHg, M.W. by B.P.) The original reaction also gives hydrazodicarboxylic ethyl ester.

The formation of this substance from hydrazine carboxylic ester bears a close relation to the reactions by which Emil Fischer obtained

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[2] Diels and Uthemann, *Ber.* 53 (1920), 723.

mercury diethyl and mercury diphenyl during the oxidation of ethyl hydrazine and phenyl hydrazine by mercuric oxide.[3]

The corresponding *methyl ester* is prepared in the same way as the ethyl compound and has similar properties. M.P. 215°. (CHNHg).

Mercurated Acetic Acids.[4]

Bromomercuri-acetic acid, $BrHg — CH_2CO_2H$.

Bromine and potassium hydroxide are allowed to react on a methyl alcohol solution of ethanol mercuric bromide, $HOCH_2 — CH_2 — HgBr$, obtained from the reaction product of ethylene and basic mercuric nitrate. The mercurated acetic acid forms a white crystalline precipitate. (CHBrHg). M.P. 198°. When a solution in potassium cyanide is treated with hydrogen sulfide mercuric sulfide is obtained at once. The filtrate is evaporated to dryness and the residue is extracted with absolute alcohol to extract the potassium acetate. This is identified by changing to silver acetate.

Potassium iodide reacts with bromomercuri acetic acid giving a yellow iodide which is not changed by 20 per cent nitric acid, dilute hydrochloric acid, or ammonium hydroxide.

Anhydro hydroxymercuri-acetic acid.[5]

Mercuric acetate heated above its melting point gives a compound which is probably a mercurated acetic acid or an anhydride of such a substance.

A substance which is probably a trimolecular form of this anhydride is obtained by treating mercury malonic ester with sodium hydroxide for some time at 37° and then precipitating with carbon dioxide.[6] (CHHg). Yield 90 per cent. It decomposes at 250° with a slight explosion. Probably the same substance is obtained by treating malonic acid with an excess of sodium hydroxide and precipitated mercuric oxide. The evidence for the trimolecular formula is that one molecule of formic acid reacts with an amount of the anhydride

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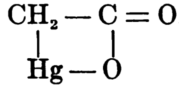
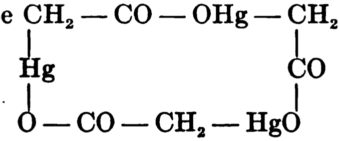
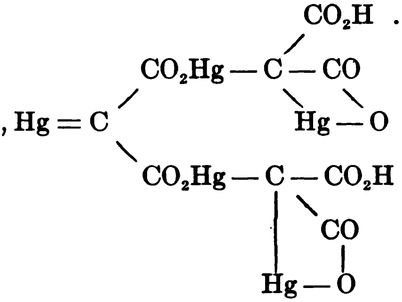
[3] E. Fischer, *Ann.* 199 (1879), 332.

[4] Hofmann and Sand, *Ber.* 33 (1900), 1340. Sand, *Ber.* 34 (1901), 1385. Dimroth, *Ber.* 35 (1902), 2853. Sand and Genssler, *Ber.* 36 (1903), 3699. Schoeller and Schrauth, *Ber.* 41 (1908), 2087. Biilmann, *Ber.* 42 (1909), 1068. Schoeller and Schrauth, *D. R. P.* 219, 966. *Chem. Zentr.* 1910 I 1078.

[5] Dimroth, loc. cit. 2870.

[6] Schoeller and Schrauth, *Ber.* 41 (1908), 2090.

corresponding to three of the single molecules,  $\begin{array}{l} CH_2 - C = O \\ \;|\qquad\;\; | \\ Hg - O \end{array}$. Thus the trimolecular anhydride would be  $\begin{array}{lcl} CH_2 - CO - OHg - & & CH_2 \\ | & & | \\ Hg & & CO \\ | & & | \\ O - CO - CH_2 - & & HgO \end{array}$. The product obtained by dissolving this in formic acid and precipitating by alcohol would have the formula, $HCO_2Hg - CH_2 - CO_2Hg - CH_2 - CO_2Hg - CH_2 - CO_2H$. (CHHg). Yield 70 per cent. Colorless crystals decomposed by heat. It is insoluble in all common solvents.

A difference of opinion exists as to the possibility of making the above anhydride from malonic acid, sodium hydroxide, and mercuric oxide. Biilmann carried out the reaction between these substances using four different sets of conditions.[7] He believes the product to have the complex structure,  $Hg = C\begin{array}{l} \diagup CO_2Hg - C(CO_2H) - CO \\ \qquad\qquad\quad \diagdown Hg - O \diagup \\ \diagdown CO_2Hg - C - CO_2H \\ \qquad\qquad\;\; | \diagdown CO \\ \qquad\qquad\; Hg - O \end{array}$ (CHHg).

Sodium salt of hydroxymercuri-acetic acid, $HOHg - CH_2CO_2Na$.[8]

The anhydride obtained from mercury malonic ester is dissolved in one molecule of sodium hydroxide for each atom of mercury and evaporated with the exclusion of carbon dioxide. The substance is obtained in small needles soluble in water but insoluble in organic solvents. Ammonium sulfide gives mercuric sulfide. Metallic copper gives no action. The solution of the sodium salt does not coagulate albumen. Heavy metal salts may be prepared by precipitation. Thus the copper salt is made by mixing solutions of the sodium compound and copper sulfate. (Cu).

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[7] *Ber.* 42 (1909), 1068.

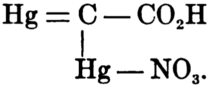
[8] Schoeller and Schrauth, loc. cit.

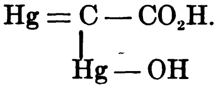
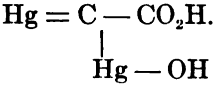
Nitratemercuri-acetic acid, $NO_3-Hg-CH_2CO_2H$.

The anhydride dissolves in fairly concentrated nitric acid and gives a precipitate of variable composition when treated with water or alcohol.

Chloromercuri-acetic acid.[9]

A double compound of the potassium salt with potassium chloride is obtained by boiling potassium monochloroacetate with mercuric oxide and water. It can be crystallized from alcohol. White matted needles. (CHClKHg). Dilute hydrochloric acid immediately gives mercuric chloride, potassium chloride, and glycollic acid. Sodium hydroxide precipitates mercuric oxide. This reaction is most unusual for a carbon mercury compound. It does not reduce ammoniacal silver solution.

Mercuri-nitratemercuri-acetic acid,  $\mathrm{Hg}=\underset{\underset{\mathrm{Hg-NO_3}}{|}}{\mathrm{C}}-\mathrm{CO_2H}$ [10].

Sodium acetate, yellow mercuric oxide, and concentrated potassium hydroxide are heated on the steam bath until the oxide disappears. The yellowish white solid is extracted with hot water and washed with 5 per cent potassium hydroxide. The solution contains the potassium salt of mercuri-hydroxymercuri-acetic acid,  $\mathrm{Hg}=\underset{\underset{\mathrm{Hg-OH}}{|}}{\mathrm{C}}-\mathrm{CO_2H}$. The insoluble substance is probably a polymer of this acid. It is dissolved in 30 per cent nitric acid and precipitated by water. The nitrate forms a yellowish white crystalline substance. (CHHg). It decomposes on heating. Hot dilute hydrochloric acid dissolves it with partial decomposition. 10 per cent potassium cyanide gives a solution of mercuric cyanide and potassium acetate. Sodium carbonate and even 5 per cent potassium hydroxide replace the nitrate group by hydroxyl without reacting with the carbonyl group. The product is a bluish white precipitate of  $\mathrm{Hg}=\underset{\underset{\mathrm{Hg-OH}}{|}}{\mathrm{C}}-\mathrm{CO_2H}$. Only a large excess of a base will dissolve the precipitate forming a salt.

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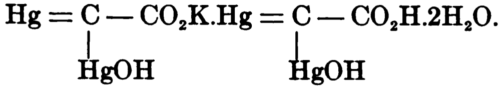
[9] Hofmann, *Ber.* 32 (1899), 880

[10] *Ibid.* 875.

Potassium salt of mercuri-hydroxymercuri-acetic acid,



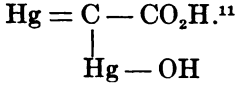
$$\mathrm{Hg} = \underset{\substack{|\\ \mathrm{HgOH}}}{\mathrm{C}} - \mathrm{CO_2K.Hg} = \underset{\substack{|\\ \mathrm{HgOH}}}{\mathrm{C}} - \mathrm{CO_2H.2H_2O}.$$

The solution in 5 per cent potassium hydroxide obtained during the preparation of the above nitrate is precipitated by dilute nitric acid as a bright yellow jelly. This is dissolved in 5 per cent potassium hydroxide using a *large excess* to avoid the formation of the insoluble polymer. The solution is treated with methyl or ethyl alcohol which gives a yellow precipitate of the acid potassium salt. ($CHKHg,H_2O$).

Dichloromercuri-acetic acid $(ClHg)_2CH - CO_2H$.

The above potassium salt is treated with 2 per cent hydrochloric acid or the original solution in 5 per cent potassium hydroxide is treated with an excess of dilute hydrochloric acid. ($CHClHg$).

Mercuri-hydroxymercuri-acetic acid,



$$\mathrm{Hg} = \underset{\substack{|\\ \mathrm{Hg - OH}}}{\mathrm{C}} - \mathrm{CO_2H}.^{11}$$

The corresponding nitrate is boiled with sodium carbonate solution. Another preparation starts with ethanol mercuric iodide, $CH_2OH - CH_2 - HgI$, obtained from ethylene and mercuric salts. This is boiled with potassium hydroxide and mercuric oxide. The residue is dissolved in 20 per cent nitric acid, filtered, and precipitated by water. The precipitate is washed with 2 per cent nitric acid and then boiled with an excess of sodium carbonate solution to form the desired acid. ($CHHg$).

As has been mentioned an insoluble polymer of this acid is formed in the reaction between sodium acetate and mercuric oxide in alkali. It remains after the extraction with 5 per cent potassium hydroxide. It dissolves in concentrated potassium hydroxide only on long boiling.

Trichloromercuri-acetic acid, $(ClHg)_3C - CO_2H$.[12]

This substance may be prepared from monochloroacetylene and mercuric chloride. It may also be made from the mercarbide, $C_2Hg_4Cl_4$, obtained from sodium acetate and alcoholic mercuric chloride.[13] When this is heated with sodium hydroxide and the solution is precipitated with dilute hydrochloric acid the trichloromercuri-acetic acid is ob-

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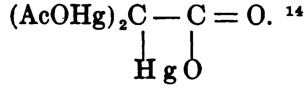
[11] Hofmann and Sand, *Ber.* 33 (1900), 1348.

[12] Hofmann, *Ber.* 31 (1898), 2217. Hofmann, *Ber.* 32 (1899), 872. Hofmann and Kirmreuther, *Ber.* 42 (1909), 4234.

[13] Hofmann, loc. cit.

tained as a white amorphous solid. (ClHg). The residue insoluble in the base contains the explosive ethane hexamercarbide.

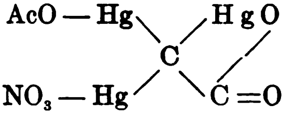
Anhydride of Hydroxymercuri-diacetoxymercuri-acetic acid,



$$\begin{array}{ll}(\mathrm{AcOHg})_2\mathrm{C} - & \mathrm{C} = \mathrm{O}.\\ \quad\quad\quad\quad\ \ | & | \\ \quad\quad\quad\quad\ \ \mathrm{Hg} & \mathrm{O}\end{array}$$ [14]

Dry mercuric acetate is heated with freshly distilled acetic anhydride until a portion tested with sodium hydroxide gives no mercuric oxide. A fine microcrystalline precipitate is obtained. (CHHg). It is insoluble in organic solvents, soluble with decomposition in hydrochloric acid and potassium cyanide, but soluble without decomposition in 20 per cent nitric acid. The hydroxide and iodide are prepared by potassium hydroxide and potassium iodide respectively.

Anhydride of hydroxymercuri-acetoxymercuri-nitratemercuri-acetic acid,



This substance is prepared by dissolving the above acetate in 20 per cent nitric acid and diluting with water. (CHNHg). Its properties are like those of the acetate.

Trihydroxymercuri-acetic acid.[15]

The acetate obtained from mercuric acetate and acetic anhydride is treated with cold 10 per cent potassium hydroxide. The solid product is washed with dilute alkali, water, and alcohol. It explodes if heated to about 200°. It is readily soluble in cold 20 per cent hydrochloric acid and in potassium cyanide solution. If heated at 160° it gives a loss corresponding to 2.5 molecules of water and one of carbon dioxide. The original substance thus contains water of crystallization.

When the acid is warmed with water and sodium amalgam for two hours, saturated with carbon dioxide, and evaporated to dryness a residue is left from which alcohol extracts sodium acetate. This is identified by changing to the silver salt.

Anhydride of hydroxymercuri-di-iodomercuri-acetic acid. (?)

The above trimercurated acid is treated with potassium iodide. (No analyses) Treatment of the iodine compound with alcohol and iodine gives iodoform and mercuric iodide.

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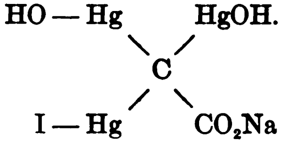
[14] Sand and Genssler, *Ber.* 36 (1903), 3707.

[15] *Ibid.* 3708.

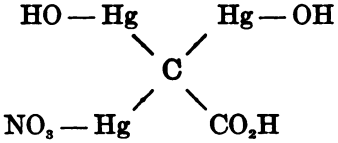
Sodium salt of dihydroxymercuri-iodomercuri-acetic acid,



[16]

Sodium acetate is heated with sodium hydroxide and mercuric iodide at 105°. The yellow leaflets of the sodium salt are purified by repeated extractions with hot dilute alkali. (ClNaHg). The substance is only slightly decomposed by hot dilute hydrochloric acid or bromine water. It is decomposed by potassium cyanide solution. The free *acid* is obtained from the sodium salt by treatment with dilute nitric acid. It forms greenish white leaflets. (CHIHg). Treatment of the acid with hot potassium iodide gives an alkaline solution.

Dihydroxymercuri-nitratemercuri-acetic acid,

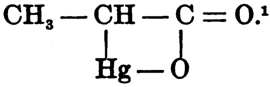


[17]

The above iodide is treated with a hot dilute silver nitrate solution. The solid product is extracted with 30 per cent nitric acid which leaves the silver iodide. The solution is diluted. The yellowish white precipitate is purified by dissolving again in nitric acid and precipitating by water. (CHNHg). It decomposes on heating. It is soluble with partial decomposition in hydrochloric acid, potassium cyanide, and potassium iodide.

Mercurated Propionic Acids.

Anhydride of α-hydroxymercuripropionic acid,



$CH_3 - \underset{\displaystyle Hg - O}{\underline{CH - C}} = O.$[18]

Hydroxymercuri methyl malonic methyl ester is boiled a short time with 2.5 moles of normal sodium hydroxide. A slight precipitate is filtered off and the filtrate is treated with a slight excess of normal sul-

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[16] Hofmann, *Ber.* 32 (1899), 878.

[17] *Ibid.*

[18] Schoeller and Schrauth, *Ber.* 42 (1909), 782. *Chem. Zentr.* 1909 I 1520. *Chem. Abst.* 4 (1911), 3018.

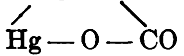
furic acid. The precipitate which forms is filtered, washed, and suspended in water. The mixture is then boiled until no more carbon dioxide escapes. The product is an amorphous powder. (CHHg). Yield 97 per cent. Heating to 150° causes decomposition with the formation of mercury and carbon. Halogen acids decompose it giving mercuric halides. Dilute sulfuric acid has no effect. Dilute nitric acid gives nitrates of the mercurated propionic acid of varying composition. The anhydride is insoluble in organic solvents but is easily soluble in alkalies giving the corresponding salts of α-hydroxymercuri propionic acid. The acid properties are too weak for it to form salts with alkaloids which might be used for its separation into optical isomers. The C — Hg linkage in this compound is unusually unstable to acids.

β-*Mercury bis-propionic acid,* $Hg(CH_2 — CH_2 — CO_2H)_2$.[19]

β-Iodopropionic ethyl ester is treated with 0.5 per cent sodium amalgam and ether in the cold. The ether solution is separated and evaporated leaving a yellow oil. This is shaken with normal sodium hydroxide and warmed. The solution is cooled and treated with a slight excess of dilute sulfuric acid. Colorless crystals separate. Yield 27 per cent. It is quickly crystallized from a large volume of hot water. (CHHg). M.P. 147-8° (corr. 148.5-149.5°), with darkening. It is easily soluble in warm alcohol, fairly soluble in hot ethyl acetate and acetone, difficultly soluble in ether and chloroform. It neutralizes two equivalents of sodium hydroxide with phenolphthalein as an indicator. It forms salts readily. The silver salt is made by treating a solution of the sodium salt with silver nitrate.

If a water solution of the acid is warmed gently with iodine in potassium iodide solution it gives a dark crystalline precipitate which appears to be a periodide.

Treatment with hot concentrated hydrobromic acid gives a solution which deposits crystals on cooling. These may be β-bromomercuripropionic acid, $BrHg — CH_2 — CH_2 — CO_2H$.

If the acid is heated with water at 100° it forms propionic acid and the *anhydride of β-hydroxymercuripropionic acid,*  (CHHg). This is almost insoluble in water and common solvents. It

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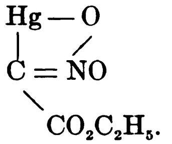
[19] Emil Fischer, *Ber.* 40 (1907), 387.

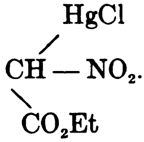
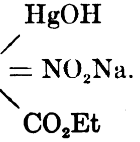
is easily soluble in alkalies and in warm dilute mineral acids. It turns gray and decomposes at 190°.

Butyric acid has been mercurated.[20]

Mercurated Nitroacetic Ester.[21]

Anhydride of hydroxymercuri aci-nitroacetic ethyl ester,



The ammonium compound of aci-nitroacetic ethyl ester is dissolved in water and treated with mercuric chloride solution. The product precipitates slowly. (Hg). It is insoluble in boiling water but soluble in base solutions. Dilute hydrochloric acid dissolves it without forming any nitroacetic ester. The product is probably chloromercurinitroacetic ester,  $CH(HgCl)(CO_2Et)—NO_2$. An excess of acid removes the mercury. The solution in sodium hydroxide probably contains the sodium aci-nitro derivative,  $C(HgOH)(CO_2Et) = NO_2Na$. Bromine in potassium bromide solution gives dibromonitroacetic ester. (Br). Potassium iodide removes the mercury as mercuric iodide indicating that the mercury is very loosely attached to the carbon.

Mercury Compounds from Unsaturated Acids.[22]

The following unsaturated acids give C — Hg compounds on treatment with mercuric salts: acrylic, crotonic, maleic, itaconic, citraconic, and allocinnamic. The product contains the groups — HgX and

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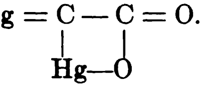
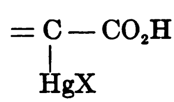
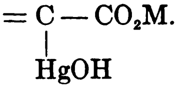
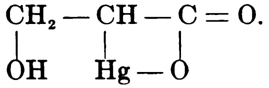
[20] Schoeller and Schrauth, *Chem Zentr.* 1910 I 1678. *Chem. Abst.* 4 (1911), 3015, 3018.

[21] Prager, *Monatsh.* 33 (1912), 1286.

[22] Billmann, *Ber.* 35 (1902), 2571. *D. R. P.* 228,877 Fraenkel, *Arzneimittelsynthese,* 4th Ed. 666.

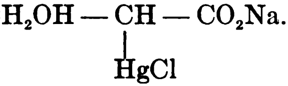
— OH added to the double bond of the original molecule. No mercury compounds are given by the transisomers such as cinnamic, mesaconic, and fumaric acids. Esters of unsaturated acids such as methyl cinnamate, ethyl oleate, triolein, and lecithin give mercury compounds when treated with mercuric salts in alcohol. In this case the groups added are — HgX and — OR. In the α-β unsaturated acids and esters the mercuri group takes the α position. Treatment with alkali and then with sulfuric acid gives anhydrides or inner salts containing the grouping  $=\underset{\substack{|\\ \text{Hg}}}{\text{C}}-\underset{\substack{|\\ -\text{O}}}{\text{C}}=\text{O}$. These anhydrides are soluble in acids, bases, and alkaline carbonates giving salts of the types  $=\underset{\substack{|\\ \text{HgX}}}{\text{C}}-\text{CO}_2\text{H}$ and  $=\underset{\substack{|\\ \text{HgOH}}}{\text{C}}-\text{CO}_2\text{M}$.

Anhydride of α-hydroxymercuri-β-hydroxypropionic acid,



$$\underset{\substack{|\\ \text{OH}}}{\text{CH}_2}-\underset{\substack{|\\ \text{Hg}}}{\text{CH}}-\underset{\substack{|\\ -\text{O}}}{\text{C}}=\text{O}.$$

Acrylic acid is treated with an acid solution of mercuric sulfate. When alcohol is added to the mixture a white smeary precipitate results. Longer treatment with alcohol renders this granular and suitable for filtration. It is very hygroscopic. It appears to have the formula $\text{C}_{12}\text{H}_{18}\text{O}_{12}\text{Hg}_4(\text{SO}_4)$. If boiled with water it gives a soluble sulfate and the anhydride. (CHHg).

The anhydride can also be made by boiling one molecule of yellow mercuric oxide with acrylic acid. When the anhydride is treated with potassium iodide about one equivalent of potassium hydroxide is formed. This indicates that the C — Hg linkage is very easily broken in this case. The anhydride is very slightly soluble in water even on heating. It is easily soluble in acids, alkalies, and alkali carbonates. Ammonium hydroxide and ammonium sulfide give mercuric sulfide. Sodium chloride and ammonium chloride dissolve the anhydride without giving an alkaline solution. These solutions probably contain salts of the type  $\text{CH}_2\text{OH}-\underset{\substack{|\\ \text{HgCl}}}{\text{CH}}-\text{CO}_2\text{Na}$. A chloride solution does not split the C — Hg linkage as does an iodide solution.[23]

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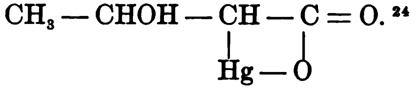
[23] Whitmore and Middleton, *J. Am. Chem. Soc.* 43 (1921), 619.

Still another method for making the anhydride is to heat mercurous acrylate forming metallic mercury, acrylic acid, and the anhydride.

Anhydride of α-hydroxymercuri-β-hydroxy-n-butyric acid,



$$\begin{array}{l} CH_3-CHOH-CH-C=O.^{24} \\ \qquad\qquad\qquad\quad | \qquad | \\ \qquad\qquad\qquad\quad Hg-O \end{array}$$

Crotonic acid is warmed with mercuric acetate solution and a trace of acetic acid, cooled, and precipitated by alcohol. The anhydride can also be made by boiling crotonic acid solution with mercuric oxide until the product is completely soluble in sodium hydroxide.

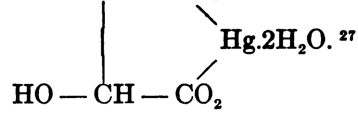
If the anhydride is dissolved in normal sodium hydroxide, treated with hydrogen sulfide, and then acidified with sulfuric acid and filtered a solution is obtained from which an oil can be extracted by ether. This oil is not crotonic acid but gives that substance when boiled with 50 per cent sulfuric acid. It is therefore β-hydroxybutyric acid formed by the replacement of the mercury by hydrogen.

Mercury derivatives of other unsaturated acids.

Oleic acid.[25]

Chaulmoogra oil and its esters.[26]

Mercuric salt of α-acetoxymercuri-β-hydroxy succinic acid,



$$\begin{array}{l} AcOHg-CH-CO_2 \\ \qquad\qquad\quad | \qquad\quad \diagdown \\ \qquad\qquad\quad | \qquad\qquad Hg.2H_2O.^{27} \\ \qquad\qquad\quad | \qquad\quad \diagup \\ \quad HO-CH-CO_2 \end{array}$$

A water solution of maleic acid gives a slight yellow precipitate. This is heated with more maleic acid forming white crystals. (CHHg). It is insoluble in water and alcohol, soluble in acids, even in acetic acid if not too dilute. It is soluble in alkalies with the precipitation of part of the mercury as the oxide. Sodium chloride dissolves it with a slight acid reaction. Potassium iodide dissolves it with the formation of almost exactly one equivalent of base indicating the splitting of

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[24] Ley, *Ber.* 33 (1900), 1014. Billmann, *Ber.* 35 (1902), 2572. Ley, *Bull. soc. chim.* (3) 33 (1905), 1320. Billmann, *Ber.* 43 (1910), 579.

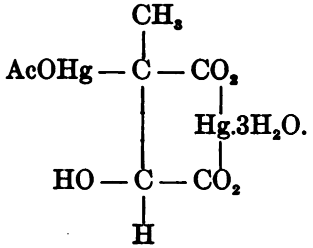
[25] Fraenkel, *Arzneimittelsynthese,* 4th Ed. 1919, 666 ff. *Realenzyk. Pharm.* VI 494. Leys, *J. pharm. chim.* (6) 21 (1905), 388. *Chem. Zentr.* 1905 I 1532. Schoeller, Schrauth, and Struensee, *Ber.* 43 (1910), 695.

[26] *D. R. P.* 245, 571. Fraenkel, loc. cit.

[27] Billmann, loc. cit. Ley, loc. cit.

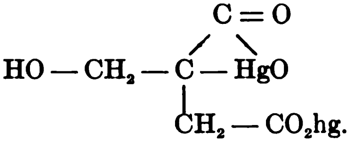
the C — Hg linkage. Treatment with sodium hydroxide and hydrogen sulfide gives a solution from which *malic acid* can be extracted in 80 per cent yield. Fumaric acid when treated with mercuric salts gives only an ordinary O — Hg compound.

Mercury salt of α-acetoxymercuri-β-hydroxy-β(?)-methyl succinic acid,



Citraconic acid is heated with mercuric acetate at 60° forming a white crystalline precipitate. (CHHg). The product is insoluble in water and alcohol but soluble in acids. Bases precipitate part of the mercury as the oxide. The alkaline solution contains the rest of the mercury which can be precipitated by hydrogen sulfide. Potassium iodide does not split the C — Hg linkage completely as it gives only .8 of an equivalent of alkali. Mesaconic acid gives only common mercuric salts from which bases precipitate all of the mercury.

Mercury salt of anhydro-α-hydroxymercuri-α-hydroxymethyl succinic acid,



[28]

Itaconic acid reacts with mercuric sulfate solution and alcohol to form a complex sulfate which changes to the desired compound on boiling with water. The product is a white insoluble substance containing $3H_2O$. (CHHg). It is easily soluble in acids and in solutions of halide salts. Potassium iodide breaks the C — Hg linkage.

Acetylenic acids and esters give mercury compounds in much the same way as the ethylene compounds.[29]

Hydroxy acids such as lactic, malic, and tartaric acids give ordinary O — Hg Salts.[30]

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[28] The symbol "hg" is used to indicate one equivalent of mercury.

[29] Ley, *Ber.* 33 (1900), 1014. *D. R. P.* 246, 207. Fraenkel, loc. cit. 667.

[30] Engelhardt and Maddrell, *Ann.* 63 (1847), 95. Brüning, *Ann.* 104 (1857), 194. Balestra, *Chem. Zentr.* 1893 I 559. *Gmelin-Kraut-Friedheim-Peters Handbuch.* V, II 454. *Merck's Index,* 1907, 282.

Mercury Derivatives of Keto Acids.

Acetoacetic ester gives mercury compounds to which a variety of formulas has been assigned.[31] None of these is conclusively proved. The compounds are decomposed by concentrated acids and potassium cyanide solution. Hydrogen sulfide gives mercuric sulfide at once. Their properties indicate the presence of a very weak C — Hg bond such as is always found when the carbon involved is alpha to a carboxyl or carbonyl group.

Other keto acids.

Levulinic acid gives ordinary mercuric salts.[32]

Tartronic acid.[33]

Acetone dicarboxylic acid gives a complex mercury compound which may very likely contain some organic mercury.[34]

Mercury Derivatives of Malonic Esters.

Mercury bis-malonic methyl *ester* $Hg[CH(CO_2CH_3)_2]_2$.[35]

Methyl malonate is shaken in the dark with water and freshly prepared yellow mercuric oxide. Yellow aggregates are formed first but in about twelve hours the product is entirely white. It is dissolved in a large amount of cold chloroform and ether is added until crystallization starts. (CHHg). It softens at 125° and melts at 127° corr. A few degrees higher it solidifies and does not melt again but decomposes at a high temperature. The crystals are slightly soluble in cold alcohol, ethyl acetate, and acetone. On standing or warming it changes to an amorphous insoluble substance which is insoluble in chloroform and is probably a polymer.

Saponification of the ester and acidification with sulfuric acid give the trimolecular anhydride of hydroxymercuri-acetic acid.

Sodium malonate when heated with mercuric oxide and alkali forms

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[31] Lippmann, *Z. Chem.* (2) 5 (1869), 29. Oppenheim, *Ber.* 10 (1877), 701. Behrend, *Z. physik. Chem.* 11 (1893), 478. Hofmann, *Ber.* 31 (1898), 2215. Ley, *Ber.* 33 (1900), 1014. Billmann, *Ber.* 35 (1902), 2585. Michael, *Ber.* 38 (1905), 2090.

[32] Ley, *Ber.* 53 (1900), 1012.

[33] Leys, *Bull. soc. chim.* (3) 33 (1905), 1316.

[34] Denigès, *Ann. chim. phys.* (7) 18 (1899), 408 ff. Ley, *Ber.* 33 (1900), 1018. Denigès, *Ann. chim. phys.* (8) 12 (1907), 396.

[35] Billmann, *Ber.* 35 (1902), 2580. Schoeller and Schrauth, *Ber.* 41 (1908), 2089; 42 (1909), 778.

an organic mercury compound. A difference of opinion exists as to the exact nature of this substance.[36]

Hydroxymercuri methyl malonic methyl ester,

$$HOHg-C(CH_3)\,(CO_2CH_3)_2.$$

Equal molecules of methyl malonic methyl ester and fresh mercuric oxide are shaken in the dark at 37° for several days. A light yellowish red product is obtained. This product contains considerable mercuric oxide which is left behind on saponifying the ester. To obtain the pure ester the mercuric oxide is removed by thorough washing with 1 per cent acetic acid. A white amorphous solid is left which is insoluble in all common solvents. The ester is washed thoroughly and dried in vacuo. (CH,Hg high). The high value for mercury may be due to partial hydrolysis. It does not melt but darkens and decomposes if heated rapidly to 235°. It is soluble in dilute acids forming salts if an excess of acid is avoided. It dissolves in bases. Ammonium sulfide blackens it at once.

Methyl malonic methyl ester reacts with mercuric chloride in alcohol giving various insoluble products including one which is regarded as "chloro dimercuri methyl malonic ester."

If the reaction between methyl malonic methyl ester and mercuric oxide is carried out at about 100° acidification of the solution gives α-hydroxymercuripropionic acid in 80 per cent yield.

The malonic ester also reacts with mercuric acetate or mercury acetamide giving products from which the mercurated propionic acid derivative can be obtained.

Succinic acid gives ordinary mercuric salts.[37]

Aminomethane disulfonic acid reacts with alkali and mercuric oxide giving mercury compounds.[38]

Citric acid gives peculiar mercury compounds which have not been studied carefully.[39]

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[36] See Mercurated acetic acids.

[37] Doepping, *Ann.* 47 (1843), 289. *Realenzyk. Pharm.* VI 506. *Gmelin-Kraut-Friedheim-Peters Handbuch.* V-II 454. *Merck's Index* 1907 281.

[38] *D. R. P.* 279, 199. Fraenkel, *Arzneimittelsynthese,* 4th Ed. 1919, 670. *Chem. Zentr.* 1914 II 1175.

[39] Vauquelin (before 1832), *Gmelin-Kraut Handbuch,* 4th Ed. 1852 V 831. *Realenzyk. Pharm.* VI 481. *Chem. Zentr.* 1913 I 743.

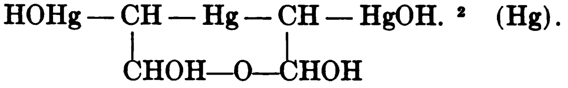
Chapter VIII.

Mercury Derivatives of Aldehydes, Ketones, and Acid Amides.

Mercury Aldehyde Compounds.

Almost all aldehydes reduce mercuric acetate to the mercurous compound in a few hours.[1]

Acetaldehyde reacts with mercuric oxide and alkali giving a substance $(C_4H_8O_5Hg_3)_x$ which is probably a polymer of a compound,

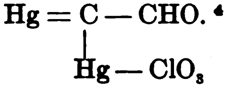


$$\begin{array}{l} HOHg - \underset{|}{CH} - Hg - \underset{|}{CH} - HgOH. \\ \quad\quad\quad CHOH - O - CHOH \end{array}$$

[2] (Hg).

The same reagents give another product which is formulated as a mercury compound of vinyl alcohol, $(CH_2 = CH —)_2Hg.HgO$.[3] (CHHg).

Mercuri-chloratemercuri-acetaldehyde, [4]



$$\begin{array}{l} Hg = C - CHO. \\ \quad\quad\; | \\ \quad\quad Hg - ClO_3 \end{array}$$

A solution of basic mercuric chlorate reacts with the calculated amount of acetaldehyde giving colorless sharp ended prisms. The substance is more explosive than mercury fulminate. It explodes even when shaken under the mother liquor. When dry it has to be handled with the greatest care as it explodes even when mixed carefully with copper oxide. (ClHg). When treated with alkalies it gives aldehyde resin.

Mercuri-nitritemercuri-acetaldehyde.[5]

This substance is obtained from the action of acetylene on a solu-

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[1] Lasserre, *J. pharm. chim.* (6) 22 (1905), 246. *Chem. Zentr.* 1905 II 1125.

[2] Auld and Hantzsch, *Ber.* 38 (1905), 2684. Hofmann, *Ber.* 31 (1898), 1904; 33 (1900), 1331.

[3] Nef, *Ann.* 298 (1897), 316.

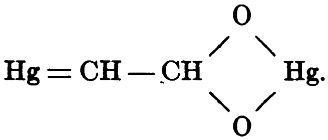
[4] Hofmann, *Ber.* 38 (1905), 2000.

[5] *Ibid.* 2004.

tion of mercuric nitrate containing an excess of potassium nitrite. It forms a bright yellow powder. (CHNHg).

Miscellaneous reactions of acetaldehyde.

Acetaldehyde reacts with an acid solution of mercuric sulfate giving a product which is formulated as $CH_3-CHO.2HgO.HgSO_4$.[6] ($CHHg,SO_4$).

Acetaldehyde reacts with a slightly alkaline solution of mercuric oxide in sodium sulfite giving a substance which is believed to be  $\mathrm{Hg{=}CH{-}CH}\!<\!\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\!>\!\mathrm{Hg}$.[7] (CHHg). Dilute nitric acid and potassium cyanide decompose it giving acetaldehyde. Apparently hydrochloric acid does not decompose it as a solution of the substance in hydrochloric acid gives no action with sodium hydroxide or potassium iodide. Sulfides give mercuric sulfide. Higher aldehydes react with the alkaline sodium sulfite solution of mercuric oxide giving mercury compounds.[8]

Alcohol treated with mercuric nitrate gives a white precipitate which is probably a tri-mercurated acetaldehyde.[9]

Mercury Compounds of Ketones.

Acetone reacts with mercury compounds giving a variety of substances to which many different formulas have been assigned. Many of these substances are written as double compounds of acetone with mercuric oxide or basic mercuric salts.
$2Me_2CO.3HgO$,[10] $4Me_2CO.6HgSO_4.9HgO$ and $Me_2CO.2HgSO_4.3HgO$,[11] $Me_2CO.2HgO$,[12] $3Me_2CO.5HgSO_4.5HgO$ and $Me_2CO.2HgSO_4.3HgO$.[13] $5Me_2CO.8HgSO_4.12HgO$.[14]

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[6] Denigès, *Ann. chim. phys.* (7) 18 (1899), 396.

[7] Leys, *Bull. soc. chim.* (3) 33 (1905), 1318.

[8] Leys, loc. cit.

[9] Biilmann, *Ber.* 35 (1902), 2588. Compare Gerhardt, *Ann.* 80 (1851), 111; Cowper, *J. Chem. Soc.* 39 (1881), 242; Hofmann, *Ber.* 31 (1898), 2783.

[10] Reynolds, *Chem. News* 23 (1871), 217. *Z. Chem.* (2) 7 (1871), 254. *Ber.* 4 (1871), 483.

[11] Oppenheimer, *Ber.* 32 (1899), 986. Hofmann, *Ber.* 31 (1898), 399.

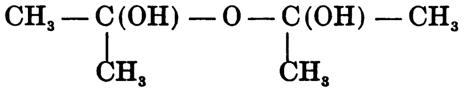
[12] Lasserre, *J. pharm. chim.* (6) 22 (1905), 246. *Chem. Zentr.* 1905 II 812, 1125.

[13] Biilmann, *Ber.* 35 (1902), 2584. Hofmann, loc. cit.

[14] Denigès, *Ann. chim. phys.* (8) 12 (1907), 401.

An extremely complex compound with ammonium chloride, mercuric chloride, and hydroxylammonium chloride has been reported.[15] It is assigned the formula $2Me_2CO.5HgCl_2.2NH_4Cl.2(NH_2OH.HCl)$.

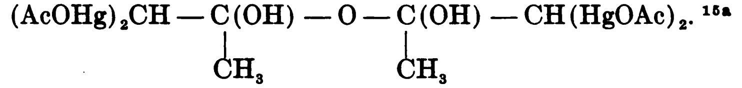
Another series of compounds of acetone is known. These are formulated as derivatives of an ether-like molecule formed by the elimination of water from two molecules of an acetone hydrate. This hypothetical substance would have the formula



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)-O-\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)-CH_3$$

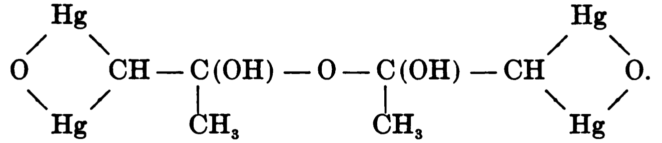
and could be called "diacetone hydrate."

Tetra-acetoxymercuri diacetone hydrate,



$$(AcOHg)_2CH-\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)-O-\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)-CH(HgOAc)_2.$$ [15a]

Dry mercuric acetate is heated with acetone at 100° for two hours. The mixture is filtered and the filtrate is evaporated to a yellow oil. This is dissolved in a little alcohol and allowed to stand. White flakes slowly separate. These are recrystallized from hot alcohol containing a little acetic acid. (CHHg). M.P. 157°. 20 per cent hydrochloric acid and potassium cyanide solution decompose the substance liberating acetone. Potassium hydroxide gives the corresponding hydroxymercuri compound. When this is dried in a vacuum it becomes the *anhydro compound,*


(CHHg).

It is insoluble in water and common solvents. It is easily soluble in dilute hydrochloric acid and potassium cyanide solution with the formation of acetone. The acetate reacts with ammonium oxalate giving a corresponding complex *oxalate*. (CHHg). A water solution of the acetate reacts with sodium chloride solution giving a precipitate of the corresponding *chloride*. (CHHg). The chloride is insoluble in water and common solvents.

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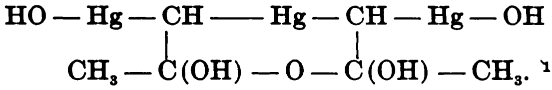
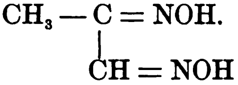
[15] Grigorowitsch, *Chem. Zentr.* 1906 I 743.
[15a] Sand and Genssler, *Ber.* 36 (1903), 3704.

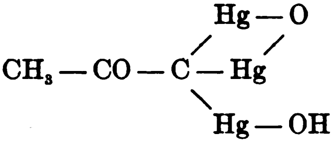
Tri-mercuri diacetone hydrate,



$$\begin{array}{l} HO-Hg-\overset{}{CH}-Hg-CH-Hg-OH \\ \qquad\quad | \qquad\qquad\qquad | \\ CH_3-C(OH)-O-C(OH)-CH_3. \end{array}$$[16]

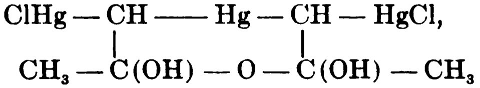
Acetone is treated with freshly precipitated mercuric oxide and barium hydroxide solution. A syrup is obtained which is soluble in water. (CHHg). It is indifferent to phenyl hydrazine and hydroxylamine. When the water soluble oil stands in contact with bases it changes to an insoluble polymer. (CHHg). Treatment of the oil with dilute hydrochloric acid gives mercuric chloride and acetone at once. Bromine gives dibromacetone which can be removed by steam distillation and changed by hydroxylamine to methyl glyoxime, $\begin{array}{l} CH_3-C=NOH \\ \quad\;\; | \\ \quad\; CH=NOH \end{array}$ The oil forms a well crystallized picrate. (Hg, H_2O, picric acid). Long boiling of either the soluble or insoluble form of the hydroxide with alkalies gives acetone and acetone mercarbide,





, (CHHg).

The corresponding *chloride,*



$$\begin{array}{l} ClHg-CH-Hg-CH-HgCl, \\ \qquad\quad | \qquad\qquad\qquad | \\ CH_3-C(OH)-O-C(OH)-CH_3 \end{array}$$

is made from the hydroxide by careful addition of dilute hydrochloric acid. It is difficultly soluble in alcohol but easily soluble in pyridine and aniline. (ClHg). It turns yellow and melts at 110°. It forms an amorphous platinichloride which decomposes at 178°. (Pt). The *bromide* is made like the chloride and has similar properties. It forms small white needles melting at 127°. (BrHg). The *iodide* is made from the base by adding potassium iodide and cold dilute acetic acid. It is more soluble in alcohol and ether than the other halides. M.P. 104°. (IHg).

Acetone treated with yellow mercuric oxide and sodium hydroxide solution at room temperature for a long time gives a white com-

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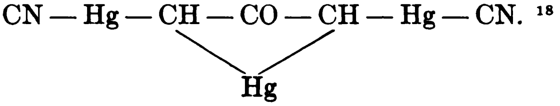
[16] Auld and Hantzsch, *Ber.* 38 (1905), 2678.

pound which reacts with dilute nitric acid forming a *mercarbide,* $C_3Hg_3H_5O(NO_3)_2$. This substance can also be made from acetone and an acid mercuric nitrate solution. When the nitrate is treated with sodium hydroxide it gives an explosive compound, $C_3Hg_3H_7O_3$.[17]

Acetone reacts with alkaline mercuric cyanide solution giving an insoluble white powder, $C_5Hg_3H_2ON_2$. (CHNHg). Dilute hydrochloric acid removes all of the mercury. It probably has the structure,



$$\begin{array}{c}\mathrm{CN-Hg-CH-CO-CH-Hg-CN.}^{18}\\ \mathrm{Hg}\end{array}$$

Acetone reduced in acid solution at a mercury cathode forms mercury di-isopropyl.[19]

Monochloracetone reacts with acid mercuric sulfate solution giving a compound which is formulated as $ClCH_2-CO-CH_3.2HgSO_4.3HgO$. (ClHg,$SO_4$). It decomposes explosively at 133°.[20]

Mercury Derivatives of Higher Ketones.

Methylethyl ketone reacts with an acid mercuric sulfate solution forming a precipitate, $4MeEtCO.6HgSO_4.9HgO$.[21] Methyl ethyl ketone also reacts with mercuric acetate much as acetone does giving a tetra-acetoxymercuri derivative of the diketone hydrate. This substance forms "an oxonium picrate" with one half molecule of picric acid. (CHNHg).

Higher ketones such as diethyl ketone, dipropyl ketone, and dibutyl ketone give mercury compounds of doubtful constitution.[22]

Acetyl acetone gives a mixture of mercury compounds.[23]

Mesityl oxide and phorone give mercury compounds which have not been studied.[24]

Allyl acetoxime reacts with mercuric acetate giving a compound which forms an iodide of the formula,

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[17] Hofmann, *Ber.* 31 (1898), 1908, 2213.

[18] Marsh and Fleming-Struthers, *Proc. Chem. Soc.* 21 (1905), 248. *Chem. Zentr.* 1906 I 229. *J. Chem. Soc.* 87 (1905), 1878; 95 (1909), 1778.

[19] Tafel, *Ber.* 39 (1906), 3626.

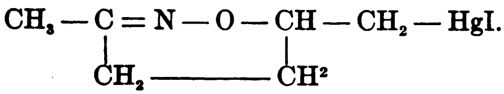
[20] Denigès, *Ann. chim. phys.* (7) 18 (1899), 400.

[21] Denigès, loc. cit.

[22] Marsh and Fleming-Struthers, loc. cit. Denigès, loc. cit. Auld and Hantzsch, loc. cit. Leys, *Bull. soc. chim.* (3) 33 (1905), 1320. Reynolds, *Chem. News* 23 (1871), 217. *Z. Chem.* (2) 7 (1871), 254.

[23] Billmann, *Ber.* 35 (1902), 2585.

[24] Hofmann and Sand, *Ber.* 33 (1900), 1340.



$$\begin{array}{l} CH_3-C=N-O-CH-CH_2-HgI.^{25} \\ \quad\;\, | \qquad\qquad\quad\;\; | \\ \quad CH_2 \text{———————} CH^2 \end{array}$$

Mercury Compounds of Amino Acids.

Mercuric acetate and other mercuric salts are much used in precipitating amino acids. The compounds obtained have the mercury attached to N, to O, or to both and are therefore not true organic mercury compounds.

Mercury Derivatives of Cyano Acids.

Hydroxymercuricyanoacetic acid.[26]

Mercuric oxide is shaken with slightly more than one molecule of cyanoacetic acid. Reaction starts at once and in two days all of the oxide is gone and a white crystalline precipitate is left. (CHNHg). It is soluble in alkalies. Ammonium cyanoacetate gives a more complicated mercury compound. Sodium cyanoacetate reacts with mercuric oxide, giving the sodium salt of hydroxymercuricyanoacetic acid. (NNaHg). The potassium and barium salts have been made and analyzed.

Hydroxymercuricyanoacetic ethyl ester.

Ethyl cyanoacetate is treated with mercuric acetate in methyl alcohol. A white crystalline precipitate of the *hydroxide* separates. This is filtered at once and washed. (CNHg). The *methyl* ester is prepared in the same way. (NHg).

a-Hydroxymercuri-a-cyanopropionic acid.

It is a yellowish white precipitate prepared from the acid and mercuric oxide. (CHNHg). It is soluble in alkalies.

Mercury Derivatives of the Acid Amides.

Acid amides readily dissolve mercuric oxide forming N — Hg compounds of the general formula $(R-CO-NH-)_2Hg$, which are usually water soluble. The N — Hg linkage is easily split by dilute acids, sulfides, and iodides, but usually not by bases.[27] It is often said that

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[25] Sand, *Ann.* 329 (1903), 181.

[26] Petterson, *J. prakt. Chem.* (2) 86 (1912), 458.

[27] Ley and Schaefer, *Ber.* 35 (1902), 1309. B. Fischer and Grützner, *Arch. Pharm.* 232 (1894), 329. *Chem. Zentr.* 1894 II 738. Dessaignes, *Ann.* 82 (1852), 281.

the linkings C — Hg and N — Hg differ entirely in their stability toward various reagents. This statement is true only in the most general way. There are many C — Hg compounds which react as rapidly with iodides as do the mercury acid amides. The mercurated phenols for example react with potassium iodide giving phenol, potassium hydroxide, and mercuric iodide in the same way that mercury acetamide will give acetamide, potassium hydroxide, and mercuric iodide.[28]

Mercury formamide exists only in solution.[29]

A solution of mercuric oxide in the least possible amount of formamide poured into a large amount of alcohol gives a white amorphous precipitate of N-hydroxymercuriformamide, H — CO — NH — HgOH. When this is dissolved in hydrochloric acid it gives compounds, 2HCONH - HgCl.3HCl and HCONH - HgCl.HCl.

Mercury acetamide, $(CH_3CONH—)_2Hg$.[30]

Yellow mercuric oxide is added to melted acetamide in a porcelain dish. The temperature is slowly raised to 180°. All the oxide dissolves giving a slightly yellow solution. The melt is cooled and dissolved in water, filtered, and evaporated to dryness on the water bath. The product is recrystallized from methyl alcohol. Yield 80 per cent. M.P. 195°.

The preparations and properties of the other mercury acid amides are so similar to those of mercury acetamide that they will simply be listed with their references.

Mercury monochloroacetamide.[31]

Mercury cyanoacetamide. The compound formed from cyanoacetamide may have the mercury attached to carbon instead of to nitrogen.[31a]

Mercury nitroacetamide.[32]

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[28] Whitmore and Middleton, *J. Am. Chem. Soc.* 43 (1921), 622.

[29] Fischer and Grützner, loc. cit.

[30] Strecker, *Ann.* 103 (1857), 324. W. Morkownikoff, *Z. Chem.* (1) 6 (1863), 535. Oppenheim and Pfaff, *Ber.* 7 (1874), 624. André, *Compt. rend.* 102 (1886), 116. Ley and Kissel, *Ber.* 32 (1899), 1359. Schoeller and Schrauth, *Ber.* 42 (1909), 784. Franklin, *Am. Chem. J.* 47 (1912), 393.

[31] Menschutkin and Jermolajeff, *Z. Chem.* (2) 7 (1871), 5. Francesconi and de Plato, *Gazz. chim. ital.* 33 I (1903), 228. *Chem. Zentr.* 1903 II 24.

[31a] Ley and Schaefer, loc. cit.

[32] Prager, *Monatsh.* 33 (1912), 1289.

Mercury propionamide.[33]
Mercury butyramide.[34]
Mercury oxamide.[35]
Mercury succinamide.[36]
Mercury phenyl succinamide.[36a]
Mercury succinimide.[37] Conductivity measurements indicate that the linkage Hg — N = of the mercury imides is more stable than the linkage Hg — NH — of the corresponding amides.
Mercury tartramide.[38]
Mercury fumaramide.[39]
Mercury urea compounds.[40]
Mercury compounds of diethyl barbituric acid.[41]
Mercury compounds of violuric acid.[42]

Mercury Derivatives of Dithiocarbamine Compounds.

The treatment of various amino compounds with carbon disulfide gives di-thiocarbamine derivatives from which S — Hg compounds are easily prepared. A typical example of this reaction is shown by the reaction of methylaminoacetic ethyl ester with carbon disulfide and ether giving a complex compound which reacts with mercuric chloride forming a mercury compound which on saponification gives the substance $Hg(—S—CS—N(CH_3)—CH_2—CO_2Na)_2$.[43]

Other N — Hg Compounds.

Camphorimide forms a mercury compound with properties resembling those of mercury succinimide.[44]

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[33] Ley and Fischer, *Z. anorg. Chem.* 82 (1913), 336. Sestini, *Z. Chem.* (2) 7 (1871), 35.

[34] Dessaignes, loc. cit. 234. Ley and Schaefer, *Ber.* 35 (1902), 1812.

[35] Ley and Schaefer, loc. cit. Schutz, Marsh, and Geuther, *Z. Chem.* (2) 4 (1868), 303.

[36] Ley and Kissel, loc. cit. Menschutkin, *Ann.* 162 (1872), 171.

[36a] Menschutkin, loc. cit.

[37] Ley and Schaefer, loc. cit. Menschutkin, loc. cit. Landsberg, *Ann.* 215 (1882), 209. Dessaignes, loc. cit.

[38] Grote, *Ann.* 130 (1864), 203.

[39] Dessaignes, loc. cit.

[40] Dessaignes, loc. cit. Novak, *Chem. Zentr.* 1873 154. Pflüger, *Chem. Zentr.* 1888 559. Pesci, *Z. anorg. Chem.* 15 (1897), 231. Ley and Schaefer, loc. cit. Neuberg and Kerb, *Biochem. Z.* 40 (1912), 506.

[41] Lami, *Chem. Abst.* 10 (1916), 2613.

[42] Auld, *J. Chem. Soc.* 91 (1907), 1046.

[43] Poulenc Frères, *D. R. P.* 235, 356. *Chem. Zentr.* 1911 II 170.

[44] Ley and Schaefer, loc. cit.

Uric acid forms a variety of mercury compounds.[45]

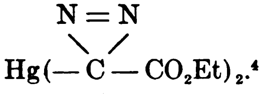
Theobromine and theophylline heated with mercuric acetate or mercuric oxide give mercury compounds which are stable to ammonium sulfide indicating that they are C — Hg compounds.[46]

Mercuric cyanide. Opinions differ as to whether mercuric cyanide is a C — Hg or an N — Hg compound.[47]

Its very slight activity with acids would indicate the C — Hg linkage. The fact that it is practically as transparent to light as pure water also indicates the C linkage as a high degree of transparency is associated with it more than with the N — Hg linking.[48]

Mercury Derivatives of Diazoacetic Esters.

Mercury bis-diazoacetic ethyl ester,



[49]

The calculated amount of mercuric oxide is dissolved in diazoacetic ethyl ester. The product is extracted with ether in which the mercury compound is readily soluble. (CHNHg). M.P. 104°. It explodes on concussion. It is volatile with steam with partial decomposition. The *methyl* ester is prepared in a similar way. It is less soluble in ether than the ethyl ester. (N). M.P. 123°, with slight decomposition. Treated with hydrogen sulfide it gives mercuric sulfide and a compound containing 11.8 per cent nitrogen whereas diazoacetic ester contains 24.6 per cent. This compound has not been identified.

Mercury diazoacetic ester reacts with water giving metallic mercury, nitrogen, and a clear solution containing alcohol, oxalic acid, and glycollic acid.

[45] Gmelin-Kraut-Friedheim-Peters, *Handbuch,* V-II 455.

[46] Fraenkel, *Arzneimittelsynthese,* 4th Ed. 1919, 676.

[47] Kieseritzky, *Z. physik. Chem.* 28 (1899), 406. Ley and Schaefer, *Z. physik. Chem.* 42 (1903), 704.

[48] Ley and Fischer, *Z. anorg. Chem.* 82 (1913), 337.

[49] Curtius and Buchner, *J. prakt. Chem.* (2) 38 (1888), 411. Buchner, *Ber.* 28 (1895), 216.

Chapter IX.

Mercury Derivatives of Aromatic Hydrocarbons and Nitro Compounds.

Mercury Phenyl Compounds.

Mercury Diphenyl.

Preparation.

1. From bromobenzene and sodium amalgam.[1]

Equal volumes of 120-140° xylene and bromobenzene are mixed with one-tenth volume of ethyl acetate and heated with an excess of 2.7 per cent sodium amalgam in an oil bath at 110° and then at about 130° for eight hours. The mixture is filtered hot and then repeatedly extracted with hot benzene. All the solutions are combined and evaporated on the steam bath and then on the oil bath up to 160°. It is best to carry out the latter part of the distillation under diminished pressure. The residue is poured out and allowed to cool. The crystals which form are washed with cold alcohol as long as any color is removed. The residue is almost pure white. The yield with 1 per cent amalgam is given as 27 per cent and that with 2.7 per cent amalgam as 46 per cent. The better yield with the more concentrated amalgam is in sharp contrast to the results with aliphatic halides.

Some mercury diphenyl is obtained as a by-product in the action of phenyl bromide, ethyl chloroformate, and sodium amalgam forming ethyl benzoate.[2] It has been suggested that the mercury diphenyl is an intermediate product in the formation of the ester. Apparently the action of ethyl chloroformate and mercury diphenyl has not been studied.

2. From bromobenzene, mercuric chloride, and sodium.[3]

This reaction carried out in benzene gives mercury diphenyl. It

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[1] Dreher and Otto, *Ber.* 2 (1869), 542. *Ann.* 154 (1870), 94. Ladenberg, *Ann.* 173 (1874), 151. Michaelis, *Ann.* 181 (1876), 290. Aronheim, *Ann.* 194 (1878), 148.

[2] Wurtz, *Compt. rend.* 68 (1869), 1300. *Ann. Spl.* 7 (1870), 125.

[3] Michaelis and Reese, *Ber.* 15 (1882), 2877.

seems possible that this reaction could be developed as the best way for making mercury diphenyl as the difficulty of bringing the bromobenzene in contact with the amalgam might be overcome in this way.

3. From phenyl arsenious oxide and mercuric chloride.[4]

A solution of $C_6H_5 — AsO$ in sodium hydroxide is heated with mercuric chloride forming mercury diphenyl.

4. From phenyl magnesium bromide and mercuric chloride.[5]

The Grignard reagent from 25 gm. of bromobenzene boiled with the calculated amount of mercuric chloride in ether for 1 hour gives 7.5 gm. of mercury diphenyl.

5. From phenyl hydrazine and mercury compounds.[6]

10 gm. of phenyl hydrazine heated with mercuric oxide gives 4 gm. of mercury diphenyl. Mercury acetamide acts the same as mercuric oxide.

6. From phenyl mercuric iodide and sodium amalgam.[7]

The reaction is carried out in alcohol or better in dry benzene.

7. From phenyl mercuric acetate and sodium stannite.[8]

Phenyl mercuric acetate, precipitated in finely divided form by pouring an alcoholic solution into water, is treated with an alkaline sodium stannite solution. A black solid consisting of mercury and mercury diphenyl is formed. The latter is extracted by hot benzene.

8. From di-(phenylmercuri) ammonium acetate and sulfur compounds.[9]

The compound, $(C_6H_5Hg)_2NH_2OAc$, obtained from phenyl mercuric acetate and ammonium hydroxide, is heated in alcohol with carbon disulfide, thiocarbanilide, or various thioureas. Mercury diphenyl is one of the products.

9. From phenyl mercuric bromide and potassium sulfide.[10]

Long boiling of the substances in alcohol gives mercuric sulfide, potassium bromide, and mercury diphenyl.

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[4] *D. R. P.* 272, 289. *Chem. Zentr.* 1914 I 1469. Fraenkel, *Arzneimittelsynthese,* 4th Ed. 1919, 661.

[5] Pfeiffer and Truskier, *Ber.* 37 (1904), 1127.

[6] Fischer and Ehrhard, *Ann.* 199 (1879), 332. Foster, *J. Chem. Soc.* 73 (1898), 791. Foster, *Chem. News* 78 (1898), 250.

[7] Dreher and Otto, loc. cit. 115.

[8] Dimroth, *Ber.* 35 (1902), 2853.

[9] Pesci, *Gazz. chim. ital.* 39 I (1909), 150.

[10] Dreher and Otto, loc. cit.

Properties.[11]

Mercury diphenyl forms small white glassy needles. M.P. 120° (121.8°,[12] 125-6° [13]). It is best recrystallized from hot benzene or chloroform. (CHHg). The white crystals turn yellow in light. It is insoluble in water, easily soluble in chloroform, carbon disulfide, benzene, less soluble in ether and boiling alcohol. It is slightly volatile with steam. It sublimes on heating above its melting point. It cannot be distilled under ordinary pressure as it decomposes giving mercury, benzene, diphenyl, carbon, and other products. B.P. $_{10\cdot 5}$ 204°. Its density varies from 2.29 to 2.34.

A solution of mercury diphenyl in chloroform shows no absorption bands as it is remarkably transparent to all wave lengths. It absorbs light less than does mercuric iodide whereas benzene absorbs light more than hydrogen iodide.[14] It absorbs the longer wave lengths more than does benzene.

Mercury diphenyl is toxic. It has a very irritating effect on the eyes.[15]

Reactions.

1. *With halogens.*

Dry chlorine gives a vigorous reaction forming phenyl mercuric chloride, phenyl chloride, and some mercuric chloride.[16]

Iodine in alcohol or carbon disulfide gives phenyl mercuric iodide and phenyl iodide. An excess of iodine changes the former to mercuric iodide.

Thiocyanogen, $(SCN)_2$, acts like a halogen giving phenyl thiocyanate and phenyl mercuric thiocyanate.[17]

2. *With metals.*

Sodium amalgam and alcohol or benzene give no change.

Lithium, sodium, and potassium react vigorously with mercury diphenyl either with or without solvents. Gray insoluble products are obtained.[18] This result is somewhat different from earlier work in

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[11] Dreher and Otto, loc. cit. Wurtz, loc. cit. Schroeder, *Ber.* 12 (1879), 564. Krafft and Lyons, *Ber.* 27 (1894), 1768. Purvis and McClelland, *J. Chem. Soc.* 101 (1912), 1519. Ley and Fischer, *Z. anorg. Chem.* 82 (1913), 338.

[12] *Chem. Zentr.* 1912 II 822.

[13] Foster, *J. Chem. Soc.* 73 (1898), 783.

[14] Ley and Fischer, loc. cit.

[15] Ladenberg, *Ann.* 173 (1874), 151.

[16] Dreher and Otto, loc. cit.

[17] Söderbäck, *Ann.* 419 (1919), 266.

[18] Hilpert and Grüttner, *Ber.* 46 (1913), 1679.

which sodium reacted on mercury diphenyl in benzene or ligroin solution forming a light brown precipitate of sodium phenyl.[19]

Magnesium gives magnesium diphenyl.[20]

Distillation with *zinc* gives zinc diphenyl. This reaction is better carried out by gently heating the substances for two minutes in an atmosphere of hydrogen as zinc diphenyl is very sensitive to oxygen and moisture.[21]

Heating mercury diphenyl with a large excess of *cadmium* gives cadmium diphenyl but the reaction does not run to completion. The best product obtained contains only 76 per cent of the cadmium compound.

Mercury diphenyl heated with *aluminum* in a stream of hydrogen or nitrogen gives a vigorous reaction when the temperature reaches 140°. The reaction then proceeds spontaneously with the formation of aluminum triphenyl. Only small quantities should be treated at a time to avoid the decomposition of the aluminum triphenyl by the strongly exothermic reaction.[22]

Mercury diphenyl and *bismuth* on heating give a mixture containing 41 per cent of bismuth triphenyl.

Mercury diphenyl heated to 200° with *zirconium* gives no action.[23] No action is obtained with *lead* or *tin*. Distillation of mercury diphenyl with freshly reduced *iron* or *copper* gives considerable diphenyl but no metallo-organic compounds.

3. *With halides of non-metals.*

Boron trichloride heated with mercury diphenyl several hours at 200° gives mercuric chloride and phenyl boron dichloride.[24] If this substance is heated with mercury diphenyl for 24 hours at 300° it gives diphenyl boron chloride and phenyl mercuric chloride.

Silicon tetrachloride at 300° forms phenyl mercuric chloride and phenyl silicon trichloride.[25]

Stannic chloride and mercury diphenyl react without heating. The reaction is exothermic. The reaction is best carried out in 80-100° ligroin with a short refluxing under a condenser protected by a drying

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[19] Acree, *Am. Chem. J.* 29 (1903), 588.

[20] Hilpert and Grüttner, loc. cit. Fleck, *Ann.* 276 (1893), 138.

[21] Dreher and Otto, loc. cit. Hilpert and Grüttner, loc. cit.

[22] Hilpert and Grüttner, *Ber.* 45 (1912), 2829.

[23] W. Peters, *Ber.* 41 (1908), 3173.

[24] Michaelis and Becker, *Ber.* 13 (1880), 59; 15 (1882), 180.

[25] Ladenberg, *Ann.* 173 (1874), 152.

tube. The products are phenyl mercuric chloride and diphenyl tin dichloride.[26]

Phosphorus trichloride heated with mercury diphenyl for a few hours at 180° gives phenyl mercuric chloride and phosphenyl chloride, $C_6H_5 - PCl_2$.[27]

Arsenic trichloride acts more rapidly than phosphorus trichloride. At 250° it gives phenyl dichlorarsine and mercuric chloride. Phenyl mercuric chloride also reacts with arsenic trichloride.[28] Phenyl dichlorarsine reacts with mercury diphenyl giving a small amount of triphenyl arsine and considerable diphenyl chlorarsine.[29]

Mercury diphenyl heated with antimony trichloride gives phenyl mercuric chloride and the pentavalent antimony derivatives, $(C_6H_5)_3SbCl_2$ and $(C_6H_5)_2SbCl_3$.[30]

Tellurium dichloride heated with mercury diphenyl to 225° forms phenyl chloride and mercury telluride.[31]

4. *With acid chlorides.*

Thionyl chloride warmed gently with mercury diphenyl gives a vigorous reaction forming the theoretical amount of phenyl mercuric chloride. Only a small amount of an oil containing sulfur is formed.[32]

Benzene sulfone chloride refluxed with mercury diphenyl in benzene gives no action. Heated in a tube at 160° it gives a small amount of phenyl mercuric chloride and sulfobenzide. Less than one gram of the latter substance is obtained from 20 gm. of mercury diphenyl. If no solvent is used the reaction is very violent forming metallic mercury, benzene, hydrochloric acid, and diphenyl.[33]

p-Toluene sulfone chloride heated with mercury diphenyl for 15 hours at 120° in benzene solution gives a good yield of p-tolyl mercuric chloride and a small amount of a sulfone.[34] This reaction has not been studied further.

5. *With acids.*

Dry hydrogen chloride gas acts on mercury diphenyl with evolution

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[26] Aronheim, *Ann.* 194 (1878), 148.

[27] Schwarze, *J. prakt. Chem.* (2) 10 (1874), 223. Michaelis and Graeff, *Ber.* 8 (1875), 922. Michaelis, *Ann.* 181 (1876), 291.

[28] Michaelis and LaCoste, *Ann.* 201 (1880), 196 ff.

[29] Michaelis and Link, *Ann.* 207 (1881), 195.

[30] Michaelis and Reese, *Ber.* 15 (1882), 2877. Hasenbäumer, *Ber.* 31 (1898), 2911.

[31] Krafft and Lyons, *Ber.* 27 (1894), 1768.

[32] Heumann and Köchlin, *Ber.* 16 (1883), 1626.

[33] Otto, *Ber.* 18 (1885), 246.

[34] *Ibid.* 249.

of heat and the formation of benzene and mercuric chloride. Concentrated hydrochloric acid gives the same result on heating. Fairly concentrated sulfuric acid gives similar results. Concentrated or fuming nitric acid gives mercuric nitrate and nitrobenzene. The reaction of nitric acid is violent even when the reaction is carried out in carbon disulfide solution at -15°.[35]

A solution of hypochlorous acid acts like free chlorine forming chlorobenzene and phenyl mercuric chloride.

Boiling glacial acetic gives benzene and phenyl mercuric acetate. If mercury diphenyl is heated with glacial acetic acid at 220° the products are benzene, diphenyl, a tar, and metallic mercury. No phenol or phenol ester is obtained. This result is in sharp contrast to the action of mercury dibenzyl under similar conditions forming benzyl acetate.[36] Formic, propionic, and myristic acids give benzene and phenyl mercuric salts.

6. *With acid anhydrides.*

Nitrogen tetroxide in chloroform solution gives phenyl mercuric nitrate and nitrosobenzene. Nitric oxide gives no action with mercury diphenyl. Nitrogen trioxide forms phenyl mercuric nitrate and benzene diazonium nitrate.[37]

Chlorine monoxide gives a violent reaction with mercury diphenyl forming carbon, mercuric chloride, and phenyl mercuric chloride. No diphenyl oxide is obtained.[38]

Sulfur trioxide reacts with mercury diphenyl forming mercuric benzenesulfonate. Sulfur dioxide gives no reaction in benzene solution. If it is bubbled through melted mercury diphenyl a reaction takes place. The product is not a sulfinate.[39]

7. *With mercuric salts.*

Mercury diphenyl in acetone reacts with mercuric chloride in the same solvent giving an immediate precipitate of phenylmercuric chloride. Yield 94 per cent. A similar reaction takes place in alcohol solution.[40] It is evidently unnecessary to use a high temperature in this reaction.[41]

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[35] Dreher and Otto, *Ann.* 154 (1870), 97, 124.

[36] Dreher and Otto, loc. cit. 117. Otto, *J. prakt. Chem.* (2) 1 (1870), 179. L. W. Jones, *J. Am. Chem. Soc.* 40 (1918), 1268.

[37] Bamberger, *Ber.* 30 (1897), 509.

[38] Dreher and Otto, loc. cit.

[39] Otto, *J. prakt. Chem.* (2) 1 (1870), 185.

[40] Steinkopf, *Ann.* 413 (1917), 313, 329.

[41] Dreher and Otto, *Ann.* 154 (1870), 113.

Mercury diphenyl heated with mercurous chloride to 160° in alcohol gives phenyl mercuric chloride and metallic mercury.[42]

Mercuric acetate is said not to react with mercury diphenyl in alcohol at ordinary temperature. Heated to 120°, the mixture gives phenylmercuric acetate.[43] Mercury diphenyl heated with an excess of mercuric acetate to 150° without a solvent gives a mixture of 1, 4-diacetoxymercuribenzene, 1, 2, 4-tri-acetoxymercuribenzene, and 1, 2, 4, 5-tetra-acetoxymercuribenzene.[44]

Mercuric cyanide heated with mercury diphenyl in alcohol at 120° gives phenylmercuric cyanide. The sulfocyanate gives a similar reaction.

8. *With organic halides.*

Ethylene dibromide and mercury diphenyl gives no action when refluxed. If heated in a tube for ten hours at 200° they give phenylmercuric bromide. No other products of the reaction have been identified.[45]

Mercury diphenyl heated with benzal chloride at 150° gives phenylmercuric chloride and triphenyl methane.[46] This is one of the very rare cases in which a compound with the linkage C — Hg reacts with one with the linkage X — C giving a compound having a new C — C linkage.

Heating mercury diphenyl with allyl iodide gives diallyl, phenylmercuric iodide, and diphenyl.[47]

9. *With oxidizing agents.*

Mercury diphenyl does not absorb oxygen from the air. Long boiling with benzene and silver oxide gives no change except for the formation of a minute amount of metallic silver.

Heating with potassium permanganate solution gives manganese dioxide, oxalic acid, and phenylmercuric hydroxide which can be changed to phenylmercuric chloride by hydrochloric acid.[48]

10. *With sulfur.*

When a mixture of mercury diphenyl and sulfur is heated in a retort until mercuric sulfide begins to form the reaction continues with-

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[42] Otto, loc. cit.

[43] Otto, loc. cit. 179.

[44] Pesci, *Atti. accad. Lincei* (5) 8 I (1899), 130. *Chem. Zentr.* 1899 I 734.

[45] Dreher and Otto, loc. cit. 128.

[46] Kekulé and Franchimont, *Ber.* 5 (1872), 907.

[47] Suida, *Monatsh.* 1 (1880), 715.

[48] Dreher and Otto, loc. cit. *Ber.* 2 (1869), 544. Otto, *J. prakt. Chem.* (2) 29 (1884), 137.

out further heating. The principal organic product is diphenyl sulfide. Some thiophenol is formed. Any excess of sulfur remains unchanged. If the mercury diphenyl is dissolved in alcohol no reaction takes place with sulfur below 140°. At that temperature mercuric sulfide and diphenyl sulfide are formed.[49]

11. *With other metallophenyl compounds.*

The various equilibrium systems involving the phenyl derivatives of mercury, bismuth, antimony, and tin have been studied. No evidence of the existence of molecular complexes is found.[50]

12. *With aromatic iodidechlorides.*

Mercury diphenyl mixed with phenyl iodidechloride and water forms diphenyl iodonium chloride, $(C_6H_5)_2I — Cl$, and phenylmercuric chloride or mercuric chloride depending on the amount of the iodidechloride used. Similar results are obtained with the iodidechlorides of o- and p-tolyl and beta naphthyl.[51]

13. *With N-halogen acid amides.*[52]

N-Bromoacetamide heated with mercury diphenyl in dry benzene gives phenyl mercuric bromide, benzene, and methyl isocyanate. The latter is identified by its action with aniline forming monophenyl urea. The reaction will also take place at room temperature if the mixture is left for a few minutes in direct sunlight. In this reaction the mercury diphenyl obviously reacts with the molecule of hydrobromic acid which is easily split off from the bromoamide.

Similar reactions take place between mercury diphenyl and bromoamides of the following acids, benzoic, o-, m-, and p-nitrobenzoic acids.

N-Chloroacetanilide is incapable of losing a molecule of acid and does not react with mercury diphenyl even on boiling the mixture in dry benzene for 14 hours.

Other Phenyl Mercuric Compounds.

Phenylmercuric hydroxide.

This substance is obtained by refluxing phenylmercuric chloride and moist silver oxide in alcohol. The filtrate from the silver chloride is evaporated leaving small white rhombic prisms. The hydroxide

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[49] Dreher and Otto, loc. cit.

[50] Cambi, *Atti. accad. Lincei* (5) 21 I (1912), 773. *Chem. Zentr.* 1912 II 822.

[51] Willgerodt, *Ber.* 31 (1898), 915.

[52] Kharasch, *J. Am. Chem. Soc.* 43 (1921), May ?

is slightly soluble in cold water, more in hot, and is soluble in alcohol and benzene. In purifying the compound air must be excluded as it absorbs carbon dioxide readily. When heated it softens at 160° but does not melt entirely at 200°. Apparently a new compound is formed during the heating. If it is placed in a bath at 200° without preliminary heating it melts but immediately solidifies and does not melt again. The hydroxide is a strong base as its water solution is strongly alkaline, absorbs carbon dioxide, and liberates ammonia from ammonium salts. It reacts with acids forming salts of C_6H_5Hg—. It precipitates aluminum hydroxide from aluminum salts.[53]

The hydroxide is also obtained by the oxidation of mercury diphenyl with potassium permanganate. The filtrate from manganese dioxide is an alkaline liquid from which the base can be extracted by benzene.[54]

Phenylmercuric chloride.

Preparation.

1. From benzene.

Mercuric acetate, glacial acetic acid, and thiophene-free benzene are heated in a pressure flask for five hours at 100°. After cooling the mixture is filtered and the residue is washed with benzene. This residue consists of polymercurated benzenes and mercurous acetate. The filtrate and washings are evaporated to small volume and treated with alcoholic calcium chloride to change the acetate to the less soluble chloride. The product is washed with hot water.[55]

2. From benzene sulfinic acid.

When this substance is heated with one molecule of mercuric chloride in alcohol until no more sulfur dioxide is evolved a small amount of phenylmercuric chloride is obtained. It can be separated from any metallic mercury formed in the reaction by dissolving in pyridine, filtering, and reprecipitating with water.[56]

3. From mercury diphenyl and mercuric chloride or mercurous chloride in alcohol or acetone.[57]
4. From phenyl boric acid heated with mercuric chloride and water.[58]

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[53] Otto, *J. prakt. Chem.* (2) 1 (1870), 183.
[54] Otto, *J. prakt. Chem.* (2) 29 (1884), 136.
[55] Roeder and Blasi, *Ber.* 47 (1914), 2751.
[56] Peters, *Ber.* 38 (1905), 2567.
[57] Dreher and Otto, loc. cit. Otto, loc. cit. Steinkopf, *Ann.* 413 (1917), 313.
[58] Michaelis and Becker, *Ber.* 15 (1882), 182.

5. From triphenyl stibine heated with mercuric chloride.[59]
6. From mercury diphenyl and chlorine.[60]
7. From mercury diphenyl and hypochlorous acid or chlorine monoxide.
8. From mercury diphenyl and thionyl chloride.
9. From phenylmercuric hydroxide and hydrochloric acid.
10. From mercury diphenyl and phosphorus trichloride.
11. From mercury diphenyl and zirconium chloride.[61]
12. From mercury diphenyl and silicon chloride.
13. From mercury diphenyl and stannic chloride.
14. From mercury diphenyl and antimony trichloride.
15. From mercury diphenyl and benzene sulfone chloride. Yield poor.
16. From mercury diphenyl and benzal chloride.

Properties.

Phenylmercuric chloride forms white satiny leaflets. ($CHClHg$). M.P. 251°. It is slightly soluble in hot alcohol, benzene, and pyridine, slightly soluble in ether. It sublimes on gentle heating.

A number of statements have been made about this substance which are probably incorrect.[62] These are that its water solution has an acid reaction, and that it is soluble in bases and carbonates giving carbon dioxide with the latter.

Reactions.

1. Moist silver oxide and alcohol give a solution of phenylmercuric hydroxide.[63]

2. Dry silver oxide reacts with the dry substance forming mercury diphenyl, mercuric oxide, and silver chloride.[64] This is a most unusual formation of mercury diphenyl.

3. With arsenic trichloride. Phenylmercuric chloride reacts with arsenic trichloride at 100° forming phenyl dichlorarsine.[65] The statement that this reaction does not take place is untrue.[66]

4. Antimony trichloride does not react even at 200°.[67]

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[59] Michaelis, *Ann.* 233 (1886), 49.

[60] The references for this and the following methods have been given under Mercury Diphenyl.

[61] Peters, *Ber.* 41 (1908), 3173.

[62] Dreher and Otto, *Ann.* 154 (1870), 126.

[63] Otto, loc. cit.

[64] Otto, *J. prakt. Chem.* (2) 1 (1870), 184.

[65] Roeder and Blasi, *Ber.* 47 (1914), 2750.

[66] Michaelis, *Ann.* 201 (1880), 197, 217.

[67] Roeder and Blasi, loc. cit. Michaelis and Reese, *Ber.* 15 (1882), 2877.

5. With sodium iodide. The only product is phenylmercuric iodide. No mercury diphenyl is obtained. The cold acetone solution of the chloride and sodium iodide is allowed to stand 24 hours and poured into water.[68]

6. With iodidechlorides. The same products are obtained as with mercury diphenyl.[69]

7. With the Grignard reagent. Benzyl magnesium chloride reacts with phenylmercuric chloride but gives dibenzyl instead of any of the expected products.[70]

8. With sulfides. Ammonium sulfide gives no action in the cold. Long boiling with sodium sulfide gives mercury diphenyl and mercuric sulfide.[71]

Phenylmercuric bromide.

Preparation.

1. From the Grignard reagent.

Phenyl magnesium bromide in ether is treated with the calculated amount of powdered mercuric bromide in small portions and then the mixture is boiled for 4 hours. The mixture is cooled, decanted, and the residue is boiled with three portions of 1 per cent hydrochloric acid to remove any mercuric bromide. The residue is washed with water, alcohol, and ether, dried at 100° and then recrystallized from pyridine. The pyridine mother liquor is heated to boiling and treated with water to precipitate the rest of the bromide. Total yield 93 per cent.[72]

2. From mercury diphenyl and bromine.

3. From mercury diphenyl and mercuric bromide in alcohol at 120°.[73]

4. From ethylene dibromide and mercury diphenyl heated at 200°.

Properties.

Phenylmercuric bromide forms white rhombic tablets of satiny luster. M.P. 276° (not 291°).[74] It is insoluble in water, barely solu-

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[68] Steinkopf, loc. cit.

[69] Willgerodt, *Ber.* 31 (1898), 917.

[70] L. W. Jones, *J. Am. Chem. Soc.* 40 (1918), 1268.

[71] Heumann and Köchlin, loc. cit.

[72] Hilpert and Grüttner, *Ber.* 46 (1913), 1686.

[73] Dreher and Otto, loc. cit.

[74] Otto, *J. prakt. Chem.* (2) 1 (1870), 186.

ble in cold alcohol and benzene, more soluble on heating, and soluble in hot pyridine. It sublimes on careful heating. (BrHg).

Reactions.

1. With the Grignard reagent. Phenylmercuric bromide acts with an excess of phenyl magnesium bromide giving only a 40 per cent yield of mercury diphenyl.[75] An excess of benzyl magnesium bromide gives mercury dibenzyl instead of the expected "mixed" compound, $C_6H_5 — Hg — CH_2 — C_6H_5$.[76]

2. With ethylene dibromide. No reaction takes place even in sealed tubes at 250°.[77]

Phenylmercuric iodide.

Preparation.

1. From mercury diphenyl and mercuric iodide in alcohol at 120°.[78] This reaction can be brought about by simply refluxing the substances in alcohol until the red color of the mercuric iodide has disappeared. The phenylmercuric iodide obtained is practically pure.[79]
2. From mercury diphenyl and iodine in carbon disulfide.
3. From phenylmercuric cyanide and iodine.[80]

Properties.

Phenylmercuric iodide forms rhombic tablets of satiny luster. (I). It is unchanged by light. M.P. 266°. It is insoluble in water, almost insoluble in cold alcohol, ether, and benzene, more soluble hot, soluble in chloroform, and still more so in carbon disulfide. Gentle heating sublimes part of the substance and decomposes the rest giving mercuric iodide. The other products have not been identified.[81]

Reactions.

1. With sodium amalgam. Phenylmercuric iodide reacts with sodium amalgam in dry benzene or even in alcohol giving mercury diphenyl. Metallic sodium gives sodium amalgam, sodium iodide, and a brown insoluble product which is probably sodium phenyl.[82]

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[75] Hilpert and Grüttner, loc. cit. 1679.
[76] Hilpert and Grüttner, *Ber.* 48 (1915), 907.
[77] Dreher and Otto, loc. cit. 129.
[78] Dreher and Otto, loc. cit.
[79] Whitmore, unpublished results.
[80] Otto, *J. prakt. Chem.* (2) 1 (1870), 182.
[81] Dreher and Otto, loc. cit. 109.
[82] Dreher and Otto, loc. cit. 93, 115.

2. With iodine. The reaction in alcohol or carbon disulfide gives phenyl iodide and mercuric iodide.

Phenylmercuric formate.

Mercury diphenyl is dissolved in hot concentrated formic acid and the solution is poured into water. The precipitate is recrystallized from hot formic acid. Small glassy tablets. M.P. 171°.

Phenylmercuric acetate, Acetoxymercuribenzene.

Preparation.

1. From mercury diphenyl and glacial acetic acid.
2. From mercury diphenyl and mercuric acetate in alcohol at 120°.
3. From phenylmercuric iodide and silver acetate in cold alcohol.
4. From benzene by direct mercuration.

Mercuric acetate does not react with boiling benzene. The two substances react when heated to 100-110°. The acetate is hard to purify and is usually converted to the less soluble chloride.[83]

Properties.

Phenylmercuric acetate forms small, white rhombic prisms of glassy luster. M.P. 149°. It is little soluble in cold water, more soluble hot, soluble in glacial acetic acid, benzene, and alcohol. It can be recrystallized from water or alcohol.

Reactions.

1. On heating. Heating at 150° decomposes phenylmercuric acetate with the formation of carbon, mercury, benzene, acetic anhydride, acetic acid, and diphenyl.[84]

2. With acids. Boiling with hydrochloric acid or dilute sulfuric acid gives benzene and mercuric salts.

3. With sodium amalgam. In the presence of water the products are mercury, benzene, and sodium acetate.

4. With halogens. An aqueous solution warmed with iodine gives mercuric iodide, phenyl iodide, and acetic acid. Some iodine pentoxide is also formed.[85]

5. With sulfides. Aqueous or alcoholic solutions treated with hydrogen sulfide give a heavy white precipitate of $(C_6H_5Hg)_2S$ which

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[83] See under preparation of Phenylmercuric chloride.

[84] Dreher and Otto, loc. cit. 122.

[85] Dreher and Otto, loc. cit. 120.

turns gray and then black on standing. Ammonium sulfhydrate in tubes at 100° gives mercuric sulfide, benzene, and acetic acid.

6. With sulfur. Heating phenylmercuric acetate with sulfur forms mercuric sulfide, benzene, acetic acid, acetic anhydride, diphenyl sulfide, and a crystalline sulfur compound of unknown composition.[86]

7. With arsenic trichloride. The acetate acts as well as the chloride forming phenyl dichlorarsine.[87]

8. With sodium stannite. A suspension of the acetate in water reacts with sodium stannite solution forming mercury diphenyl and metallic mercury.[88]

Phenylmercuric propionate.

Mercury diphenyl is dissolved in hot propionic acid. The benzene formed is distilled off. The mixture is then poured into dilute sodium carbonate solution. The precipitate is recrystallized from hot water. It is practically insoluble in cold water but is soluble in alcohol and benzene. M.P. 166° after softening slightly at 145°.

Phenylmercuric myristate, $C_6H_5 — Hg — O — CO — C_{13}H_{27}$.

Myristic acid, mercury diphenyl, and alcohol are heated to 120°. The product forms small fatty rhombic plates which are insoluble in water but soluble in hot alcohol and benzene. Boiling hydrochloric acid changes the compound to mercuric chloride, benzene, and myristic acid.

Phenylmercuric cyanide.

Mercuric cyanide and mercury diphenyl heated in alcohol at 120° form long fine rhombic prisms which are slightly soluble in hot water and more soluble in hot alcohol and benzene. M.P. 204°. Phenylmercuric cyanide can also be prepared from the iodide and silver cyanide. Heated with hydrochloric acid at 120° the cyanide gives benzene, mercuric chloride, formic acid, and ammonium chloride. Alcoholic potassium hydroxide at 120° gives metallic mercury, benzene, and potassium cyanate. Iodine gives phenylmercuric iodide and cyanogen iodide. Hydrogen sulfide first gives a white precipitate and then mercuric sulfide, hydrocyanic acid and benzene. No sulfocyanate is formed by heating with sulfur.

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[86] Dreher and Otto, loc. cit. 124.

[87] Roeder and Blasi, *Ber.* 47 (1914), 2752.

[88] Dimroth, *Chem. Zentr.* 1901 I 450.

Phenylmercuric sulfide.

The sulfide is prepared from phenylmercuric chloride and the calculated amount of sodium sulfide in alcohol. When heated it decomposes to mercuric sulfide and mercury diphenyl.[89]

Phenylmercuric nitrate.

Preparation.

It cannot be made from mercury diphenyl and nitric acid.

1. From phenylmercuric chloride and silver nitrate in alcohol.
2. From mercury diphenyl and mercuric nitrate.
3. From mercury diphenyl and nitrogen trioxide.[90]

Properties.

Phenylmercuric nitrate forms rhombic tablets, insoluble in cold water, slightly soluble hot, more soluble in hot alcohol and benzene. M.P. 176-186°.

Phenylmercuric sulfocyanate.

Preparation.

1. From mercury diphenyl and mercuric sulfocyanate heated in alcohol at 120°.

2. Phenylmercuric iodide and thiocyanogen, $(SCN)_2$, form phenylmercuric thiocyanate and iodine.[91]

Properties.

Phenylmercuric sulfocyanate forms small silky tablets, insoluble in water, soluble in hot alcohol and benzene. M.P. 231-232.5° (NSHg).

Phenylmercuric carbonate.

Phenylmercuric chloride in alcohol is treated with silver carbonate. The product forms fine white needles which are very little soluble in hot water, but fairly soluble in hot alcohol and ether. It decomposes on heating. Acetic acid liberates carbon dioxide.

Compounds of di(phenylmercuri) ammonium, $(C_6H_5Hg)_2NH_2$—.[92]

Di(phenylmercuri) ammonium acetate, $(C_6H_5Hg)_2NH_2OAc$.

Phenylmercuric acetate is dissolved in ammonium hydroxide. On

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[89] Pesci, *Gazz. chim. ital.* 29 I (1899) 394. *Z. anorg. Chem.* 32 (1902), 230.
[90] Bamberger, *Ber.* 30 (1897), 510.
[91] Söderbäck, *Ann.* 419 (1919), 268.
[92] Pesci, *Gazz. chim. ital.* 39 I (1909), 148 ff.

standing colorless laminæ separate. The complex acetate is very soluble in alcohol, especially on heating, little soluble in water, and insoluble in benzene and chloroform. The solution is alkaline and caustic to the skin. M.P. 179° (CHNHg). The acetate reacts with an excess of concentrated sodium thiosulfate giving mercury diphenyl. Refluxing with carbon disulfide in alcohol gives the same product. The corresponding complex *nitrate* is prepared by dissolving phenylmercuric acetate in ammonium hydroxide and adding a concentrated solution of ammonium nitrate. The precipitate is recrystallized from hot alcohol. (NHg). It forms very small colorless laminæ. It dissolves very slightly in water giving an alkaline reaction. M.P. 230-235° with decomposition. The *sulfate* is prepared the same as the nitrate but sodium sulfate is used as the precipitating agent as the complex sulfate forms a double compound with ammonium sulfate. The complex sulfate forms white crystals which are slightly soluble in water giving an alkaline reaction. (Hg,SO_4). It does not melt. The double salt contains one molecule of ammonium sulfate. (NHg,SO_4). The *chloride* is obtained by cooling a filtered solution of phenylmercuric chloride in hot ammonium hydroxide. The crystals which form are slightly soluble in water with an alkaline reaction. (Hg). M.P. 184° with decomposition.

Tetra(phenylmercuri) thiourea, $(C_6H_5Hg)_4N_2CS$.

Phenylmercuric acetate dissolved in ammonium hydroxide is treated with the calculated amount of thiourea in water solution. The white amorphous precipitate is carefully washed and air dried. (NSHg). It blackens at 105° but does not melt. Boiled with alcohol it gives mercuric sulfide, mercury diphenyl, and di(phenylmercuri) cyanamide, $(C_6H_5Hg)_2N-CN$.

Di(phenylmercuri) cyanamide.

It is prepared as just described or by mixing an alcoholic solution of phenylmercuric acetate with an aqueous-alcoholic solution of cyanamide. The white amorphous precipitate is insoluble in common solvents. It decomposes without melting. When heated on platinum foil it deflagrates slightly. Cold dilute hydrochloric acid gives a solution of cyanamide and a residue of phenyl mercuric chloride.

Tolylmercuric Compounds.

o-Mercury Ditolyl.

Preparation.

1. Small amounts of the ortho compound are obtained from the benzene mother liquors of the product of the action of 1.5 per cent sodium amalgam and ethyl acetate on impure bromotoluene.[93]

2. Pure o-bromotoluene (from o-toluidine) is mixed with xylene and ethyl acetate and refluxed for six hours with twice the calculated amount of 8 per cent sodium amalgam. Yield 33 per cent.[94]

Properties.[95]

o-Mercury ditolyl forms white tablet crystals which are soluble in hot benzene. (HHg). M.P. 107° (108°). B.P. 219° at 14 mm.

Reactions.

1. With boron trichloride in a tube at 180° for 12 hours it gives o-tolylboron dichloride and mercuric chloride.[96]

2. Zirconium chloride gives no reaction either dry or in presence of moisture.[97]

3. A large excess of phosphorus trichloride at 190° gives mercuric chloride and o-tolyl dichlorophosphine.[98]

4. Arsenic trichloride gives o-tolyl dichlorarsine.[99]

5. Nitrogen tetroxide at 0° acts on a chloroform solution of o-mercury ditolyl giving o-tolylmercuric nitrate and o-nitrosotoluene.[100] Nitrogen trioxide gives o-tolylmercuric nitrate, toluene o-diazonium nitrate, and a very little of the nitroso compound.

o-Tolylmercuric chloride.

Preparation.

1. From o-tolylboric acid boiled with mercuric chloride solution.[101]

2. From the benzene mother liquors from the para compound pre-

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[93] Ladenberg, *Ann.* 173 (1874), 165. Michaelis and LaCoste, *Ann.* 201 (1880), 247.
[94] Michaelis, *Ann.* 293 (1896), 292.
[95] Michaelis, *Ber.* 27 (1894), 247. Zeiser, *Ber.* 28 (1895), 1670. Ladenberg, loc. cit.
[96] Michaelis, loc. cit.
[97] Peters, *Ber.* 41 (1908), 3173.
[98] Michaelis, *Ann.* 293 (1896), 292.
[99] Michaelis and LaCoste, loc. cit.
[100] Kunz, *Ber.* 31 (1898), 1530.
[101] Michaelis, *Ber.* 27 (1894), 247.

pared by treating toluene with mercuric acetate and precipitating with sodium chloride solution. The o- and p- compounds formed in this way are hard to separate completely.[102]

3. By treating a solution of the nitrate with a chloride solution.[103]

Properties.

White crystals from alcohol. (CHHg). M.P. 146°.

Reactions.

A solution of the chloride in chloroform reacts with bromine giving a product which on oxidation gives o-bromobenzoic acid.[104]

o-Tolylmercuric nitrate.

The nitrate is prepared from o-mercury ditolyl and the oxides of nitrogen as described above. It is soluble in water. Chloride solutions precipitate o-tolylmercuric chloride.

m-Mercury Ditolyl.

m-Bromotoluene is treated with 3 per cent sodium amalgam in the usual way.[105] The m-mercury ditolyl forms colorless or light yellow needles. (CHHg). M.P. 102°. It is soluble in cold benzene, chloroform, acetone, ethyl acetate, difficultly soluble in alcohol, ether, and low boiling ligroin. It is best recrystallized from ethyl acetate. When heated with phosphorus trichloride for 12 hours at 200° it gives m-tolylmercuric chloride and m-tolyl dichlorophosphine.

m-Tolylmercuric chloride.

Preparation.

1. From m-tolyl boric acid heated with a concentrated mercuric chloride solution.[106]
2. From m-mercury ditolyl and mercuric chloride in alcohol.
3. From m-mercury ditolyl and phosphorus trichloride.

Properties.

m-Tolylmercuric chloride forms white clustered needles. (CHCl). M.P. 160°. It is easily soluble in chloroform and benzene, but difficultly soluble in alcohol. It sublimes on gentle heating.

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[102] Dimroth, *Ber.* 32 (1899), 761.

[103] Kunz, loc. cit.

[104] Dimroth, loc. cit.

[105] Michaelis, *Ber.* 28 (1895), 589. *Ann.* 293 (1896), 303.

[106] Khotinsky and Melamed, *Ber.* 42 (1909), 3094.

m-Tolylmercuric bromide.

The ditolyl compound is treated with mercuric bromide in alcohol. It is recrystallized from a large volume of hot alcohol. (Br). It forms long white needles. M.P. 184°.

m-Tolylmercuric iodide.

It is prepared like the bromide. (I). It forms white pearly leaflets. M.P. 162°.

m-Tolylmercuric salts of organic acids.

These salts are prepared by dissolving m-mercury ditolyl in the proper acid by heating and then diluting the solution with water. The *formate* forms long white needles which melt at 106°. (CH). The *acetate* is similar to the formate. It forms white needles which are difficultly soluble in cold water but readily soluble in hot water or alcohol. M.P. 84°. The *propionate* forms long white needles which are insoluble in cold water, slightly soluble in hot, easily soluble in alcohol. (CH).

p-Mercury Ditolyl.

Preparation and properties.

p-Bromotoluene is treated with sodium amalgam in the usual way.[107] The product forms needle crystals which are insoluble in water, slightly soluble in cold alcohol, more soluble in hot benzene, chloroform, and carbon disulfide. (CHHg). M.P. 238°. When heated under diminished pressure it sublimes.[108]

The best method for preparing p-mercury ditolyl makes use of the method of Peters for changing sulfinic acids to aromatic — HgCl compounds. p-Toluene sulfone chloride, obtained as a by-product in the saccharin industry, is changed to the sulfinic acid in the usual way. This is boiled with alcoholic mercuric chloride to form p-tolylmercuric chloride. This substance can be converted to p-mercury ditolyl by the reagents which usually change RHgX to R_2Hg. The best yields are obtained with potassium sulfocyanate. Even potassium iodide gives a better yield than sodium thiosulfate.[109] This series of reactions is the easiest method for obtaining a compound of the type R_2Hg in which R is an aromatic hydrocarbon residue as the yields are excellent.

[107] Dreher and Otto, *Ann.* 154 (1870), 171. Wurtz, *Compt. rend.* 68 (1870), 1298. *Ann. Spl.* 7 (1870), 128. Michaelis and La Coste, *Ann.* 201 (1880), 246.

[108] Ladenberg, *Ann.* 173 (1874), 162. Zeiser, *Ber.* 28 (1895), 1670.

[109] Unpublished results, Whitmore and L. F. Howe.

Reactions.

1. The vapors of p-mercury ditolyl passed through a hot tube give carbon, toluene, metallic mercury, and an oil which may be impure ditolyl.[110]

2. Mercuric chloride gives p-tolylmercuric chloride.

3. Hot aqueous potassium permanganate gives manganese dioxide and an alkaline solution which reacts with dilute hydrochloric acid giving p-tolylmercuric chloride.[111]

4. Nitrogen trioxide in chloroform gives p-tolylmercuric nitrate, p-toluene diazonium nitrate, and a small amount of p-nitroso toluene. Pure nitric oxide gives no reaction. Nitrogen tetroxide gives p-tolylmercuric nitrate and p-nitroso toluene.[112]

5. Boron trichloride gives p-tolyl boron dichloride.[113]

6. Halogens give the corresponding organomercuric halides and p-tolyl halides.

7. Boiling mineral acids give toluene and mercuric salts. Concentrated nitric acid gives nitrotoluenes instead of the hydrocarbon itself.[114]

8. Silicon tetrachloride at 300° gives p-tolyl silicon trichloride.[115]

9. Arsenic trichloride gives p-tolyl dichlorarsine.[116]

p-Tolylmercuric chloride.

Preparation.

1. From p-toluene sulfinic acid heated with mercuric chloride until no more sulfur dioxide is evolved.[117]

2. p-Toluene sulfone chloride heated with mercury diphenyl for 15 hours at 120° gives a good yield of p-tolylmercuric chloride.[118] This peculiar reaction has not been studied in any detail.

3. From p-tolyl boric acid heated with mercuric chloride solution.[119]

4. Toluene reluxed a short time with mercuric acetate and treated with sodium chloride solution gives a mixture of the o- and p- com-

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[110] Dreher and Otto, loc. cit.

[111] Otto, *J. prakt. Chem.* (2) 1 (1870), 185.

[112] Kunz, *Ber.* 31 (1898), 1528.

[113] Michaelis and Becker, *Ber.* 15 (1882), 185.

[114] Dreher and Otto, loc. cit.

[115] Ladenburg, *Ann.* 173 (1874), 162.

[116] Michaelis and La Coste, loc. cit. Michaelis, *Ann.* 320 (1902), 301.

[117] Peters, *Ber.* 38 (1905), 2569.

[118] Otto, *Ber.* 18 (1885), 249.

[119] Michaelis and Becker, loc. cit.

pounds which can be separated only by repeated crystallizations from benzene.[120]

5. From p-tolylmercuric nitrate and hydrochloric acid.[121]
6. From the action of hydrochloric acid on p-tolylmercuric hydroxide formed by oxidizing p-mercury ditolyl with potassium permanganate.[122]
7. From p-mercury ditolyl and mercuric chloride.[123]

Properties.

p-Tolylmercuric chloride forms silky rhombic tablets. It is insoluble in water and ether, difficultly soluble in hot alcohol, more easily in hot benzene, chloroform, acetone, and pyridine. (CHHg). M.P. 233° (not 187°).[124]

Reactions.

1. With halogens. Bromine gives p-bromotoluene melting at 28.5°.[125]
2. With sodium iodide. In cold acetone solution the only product is p-tolylmercuric iodide. No p-mercury ditolyl is formed.[126]

p-Tolylmercuric bromide.

p-Tolyl magnesium bromide is heated with mercuric chloride.[127] It is soluble in chloroform, alcohol, benzene, insoluble in cold carbon disulfide, slightly on heating. It forms thin scales of a pearly gray luster. (Br). M.P. 228°. It reacts with phenyl dichlorophosphine at 270° giving phenyl p-tolyl chlorophosphine.[128]

p-Tolyl mercuric iodide.

The iodide is prepared by treating p-tolylmercuric chloride with sodium iodide or by treating p-mercury ditolyl with iodine.[129] It forms white satiny rhombic tablets. M.P. 220°. It is insoluble in water, slightly soluble in hot alcohol, more soluble in hot benzene. It sublimes on careful heating.

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[120] Dimroth, *Ber.* 32 (1899), 761. Steinkopf, *Ann.* 413 (1917), 329.
[121] Kunz, loc. cit.
[122] Otto, *J. prakt. Chem.* (2) 29 (1884), 138.
[123] Otto, *J. prakt. Chem.* (2) 1 (1870), 185.
[124] Otto, *Ber.* 18 (1885), 249.
[125] Dimroth, *Ber.* 32 (1899), 761.
[126] Steinkopf, Ann. 413 (1917), 329.
[127] Pope and Gibson, *J. Chem. Soc.* 101 (1912), 736.
[128] Pope and Gibson, loc. cit.
[129] Steinkopf, loc. cit. Dreher and Otto, *Ann.* 154 (1870), 178.

p-Tolyl mercuric nitrate.

p-Mercury ditolyl is dissolved in chloroform and treated with the trioxide, or tetroxide of nitrogen. M.P. 187°, not sharp.

p-Tolylmercuric acetate.

Preparation.

1. From heating toluene and mercuric acetate. The product is not isolated but is transformed to the chloride.[130]
2. From p-mercury ditolyl and glacial acetic acid.

Properties.

p-Tolylmercuric acetate forms small white glassy rhombic prisms. M.P. 153°. It is practically insoluble in cold water, slightly soluble in hot water, more soluble in alcohol, carbon disulfide, and benzene.

Reactions.

It reacts like phenylmercuric acetate with inorganic acids, iodine and hydrogen sulfide.

Benzyl Mercury Compounds.

Mercury Dibenzyl.

Preparation.

Considerable difficulty was experienced in making this substance.[131] The only method which gives it is the action of a Grignard reagent with mercuric compounds.

1. From benzyl magnesium chloride and mercuric chloride.[132]
2. From benzyl magnesium chloride and benzyl mercuric chloride.[133]
3. Benzyl magnesium bromide reacts with phenyl mercuric bromide giving mercury dibenzyl instead of the expected product.[134]

Properties.

Mercury dibenzyl forms long brittle colorless needles. (CHHg). It is easily soluble in alcohol, ether, chloroform, carbon disulfide, acetic

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[130] Dimroth, loc. cit. *Ber.* 31 (1898), 2154. *Chem. Zentr.* 1901 I 450.

[131] Campisi, *Compt. rend.* 61 (1865), 861. Wurtz, *Compt. rend.* 68 (1869), 1300. Dreher and Otto, *Ann.* 154 (1870), 176.

[132] Pope and Gibson, loc. cit. Wolff, *Ber.* 46 (1913), 64. Jones and Werner, *J. Am. Chem. Soc.* 40 (1918), 1266.

[133] Jones and Werner, loc. cit.

[134] Hilpert and Grüttner, *Ber.* 48 (1915), 907.

acid, benzene and ethyl acetate, but difficultly soluble in high- and low-boiling ligroin. It has a sweet nauseating odor. It gives no absorption bands. In this remarkable transparence it resembles mercury diphenyl.[185]

Reactions.

1. Glacial acetic acid at 170° for 7 hours gives mercury, toluene, dibenzyl and benzyl acetate.[186]
2. Mercury dibenzyl reacts quantitatively with alcoholic solutions of mercuric acetate and mercuric chloride giving benzylmercuric acetate and chloride respectively.
3. Heating at 170° gives mercury and dibenzyl.

Benzylmercuric chloride.

Preparation.

1. From benzyl magnesium chloride and an excess of mercuric chloride.
2. From mercury dibenzyl and alcoholic mercuric chloride.
3. From benzyl boric acid and aqueous mercuric chloride.[187]

Properties.

Benzylmercuric chloride forms white lustrous leaflets. (CHCl). M.P. 104°. It is best recrystallized from alcohol.

Reactions.

1. Heat decomposes it.
2. With the Grignard reagent. Benzyl magnesium chloride reacts giving a good yield of mercury dibenzyl. It does not react with phenyl magnesium bromide.[188]

Benzylmercuric bromide.

Mercury dibenzyl in alcohol is treated with mercuric bromide. Leaflets. (Br). M.P. 119°.

Benzylmercuric iodide.

It is prepared like the bromide and has similar properties. M.P. 117° (I).

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[185] Purvis and McClelland, *J. Chem. Soc.* 101 (1912), 1514.

[186] Pope and Gibson, loc. cit. Jones and Werner, loc. cit. Kharasch, *J. Am. Chem. Soc.* 43 (1921), May ?

[187] Khotinsky and Melamed, *Ber.* 42 (1909), 3095.

[188] Jones and Werner, *J. Am. Chem. Soc.* 40 (1918), 1266.

Benzylmercuric acetate.

Preparation.

1. From mercury dibenzyl and mercuric acetate in alcohol.
2. From benzylmercuric chloride and silver acetate in alcohol.

Properties.

Benzylmercuric acetate forms long white needle crystals from alcohol. (CH). M.P. 126°.

Reactions.

Heating with glacial acetic acid for 7 hours at 170° gives metallic mercury and benzyl acetate as the only products.[139]

Benzylmercuric cyanide.

Mercury dibenzyl is heated with alcoholic mercuric cyanide in a tube at 130°. The product forms fine soft white needles. (CH). M.P. 124°.

Mercury Derivatives of Xylenes and Higher Benzene Homologs.

Mercuribis-3, 4-dimethyl benzene.

This substance is obtained as a by-product in the action of the corresponding bromoxylene with chloroformic ester and sodium amalgam. It is difficultly soluble in ether and hot alcohol, easily soluble in chloroform, carbon disulfide, and benzene. It is best crystallized from hot ether or alcohol from which it separates as long fine silky needles. M.P. 150°. It sublimes on careful heating.[140]

Mercuribis-2, 4-dimethyl benzene.

The corresponding bromoxylene is treated with 2 per cent sodium amalgam. It crystallizes from benzene in felted needles. M.P. 170°. It is difficultly soluble in ether and alcohol, easily soluble in hot benzene. It does not react with phosphorus trichloride up to 180°. At 230° the mixture blackens giving some of the corresponding xylyl dichlorophosphine and 2, 4-dimethylphenylmercuric chloride.[141] It reacts with arsenic trichloride forming 2, 4-dimethylphenyl dichlorarsine.[142]

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[139] Jones and Werner, loc. cit.

[140] Jacobson, *Ber.* 17 (1884), 2374.

[141] Weller, *Ber.* 20 (1887), 1719. Michaelis, *Ann.* 293 (1896), 313.

[142] Michaelis, *Ann.* 320 (1902), 330.

Mercuribis-2, 5-dimethyl benzene.

This substance is formed as a by-product in the action of the corresponding bromoxylene with sodium amalgam and chloroformic ester at 110°. It is insoluble in water, difficultly soluble in ether and hot alcohol, very soluble in chloroform, carbon disulfide, and benzene. It is best crystallized from hot toluene. It forms hard transparent prisms. M.P. 123°. It turns yellow in light. Distillation gives mercury and di-p-xylene. It reacts in the usual way with arsenic trichloride at 230°.[143]

Mercuribis-2, 4, 6-trimethylbenzene.

The corresponding bromide, bromomesitylene, is treated with sodium amalgam in the usual way. It forms silvery needles which are fairly soluble in benzene but very difficultly soluble in alcohol. M.P. 236°. It reacts with mercuric halides on heating giving the 2, 4, 6-trimethylphenylmercuric halides. All form long colorless needles. The melting points are: *Chloride* 200°, *bromide* 194°, *iodide* 178°.[144]

Mercuribis-2, 4, 5-trimethylbenzene.[144a]

2, 4, 5-Trimethylphenyl bromide is treated with 1.5 per cent sodium amalgam. It forms white prisms. M.P. 189°. It is easily soluble in benzene, chloroform, carbon disulfide, insoluble in cold alcohol, difficultly soluble in hot alcohol. It reacts with mercuric halides giving the 2, 4, 5-trimethylphenylmercuric halides which are obtained as fine white needles. The melting points are: *chloride* 201°, *bromide* 211°, *iodide* 196-7°.

Mercuribis-pentamethylbenzene.

Pentamethylphenyl bromide is treated with sodium amalgam in the usual way. The product is insoluble in alcohol, difficultly soluble in ether, easily soluble in hot xylene. It forms small prisms. M.P. 266°. Heating to a higher temperature causes decomposition.[145]

Mercuribis-4-propylbenzene.

4-*n*-propylphenyl bromide reacts with 1 per cent sodium amalgam giving a very poor yield of the mercury compound. It crystallizes from benzene or alcohol in long shiny needles. (CH). M.P. 110°.[146]

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[143] Michaelis, *ibid.*

[144] Michaelis, *Ber.* 28 (1895), 591.

[144a] *Ibid.*

[145] Jacobson, *Ber.* 22 (1889), 1220.

[146] R. Meyer, *J. prakt. Chem.* (2) 34 (1886), 103.

Mercuribis-2-methyl-5-isopropylbenzene, Mercuribis-p-cymene.

The bromide of p-cymene is treated with sodium amalgam in the usual way. The product crystallizes from alcohol in felted needles. M.P. 134°. It is soluble in alcohol, ether, benzene, xylene, and chloroform. It has a peculiar odor. It sublimes undecomposed. Cyanogen chloride does not react. Chloroformic ester gives no satisfactory result.[147] It reacts with mercuric halides in the ordinary way forming 2-methyl-5-isopropylphenylmercuric halides. The melting points are: *chloride* 156°, *bromide* 163°, *iodide* 169°.

Mercury Derivatives of Cyclohexane.

Mercuribis-cyclohexane.

A poor yield of this substance is obtained by heating cyclohexyl magnesium bromide with mercuric bromide in ether. It forms crystals which are soluble in hot alcohol. Precipitation of the hot alcoholic solution by water gives granules melting 78-9°. It is very unstable, being decomposed by light and heat. It is more soluble than mercury diphenyl. It reacts with alcoholic solutions of mercuric salts even in the cold forming cyclohexylmercuric halides. Cyclohexylmercuric compounds reduce silver and gold solutions in the presence of acid but have little effect on ammoniacal silver solution or Fehling's solution.[148]

Cyclohexylmercuric chloride.

Cyclohexyl magnesium chloride is treated with an excess of mercuric chloride. Another preparation is by the action of mercuric chloride on mercuribis-cyclohexane. It forms white leaflets when crystallized from benzene or alcohol. M.P. 164° (CClHg).

Cyclohexylmercuric bromide.

It is prepared like the chloride from the Grignard reagent. It forms white leaflets from benzene. (CBrHg). M.P. 153°. 10 gm. of benzene at 29° dissolves .3330 gm. of the substance while 10 gm. of absolute alcohol at the same temperature dissolves only 0.0424 gm. It is insoluble in water, difficultly soluble in cold alcohol and low boiling ligroin, more soluble in ether and benzene especially on heating, very soluble in pyridine, aniline, and dimethylaniline even cold. It is sensitive to light.

[147] Michaelis, *Ber.* 28 (1895), 592. Paterno and Colombo, *Ber.* 10 (1877), 1749.

[148] Grüttner, *Ber.* 47 (1914), 1655.

Cyclohexylmercuric iodide.

The corresponding bromide is dissolved in alcohol and benzene and refluxed with potassium iodide. It is recrystallized from benzene or alcohol. (CIHg). It forms white leaflets which are sensitive to light. M.P. 143°. If heated to 159° it decomposes giving bubbles and mercuric iodide.

A peculiar method of preparing the iodide is by the treatment of cyclohexyl iodide with sodium amalgam which would be expected to give mercuribis-cyclohexane.[149]

Cyclohexylmercuric cyanide.

An ether solution of mercuribis-cyclohexane is treated with an alcoholic solution of mercuric cyanide and evaported to dryness. The residue is crystallized from alcohol. (CHNHg). It forms white leaflets sensitive to light. M.P. 144°. It decomposes at 190° giving mercury. It is more soluble than the corresponding halides.

Cyclohexylmercuric sulfide.

A solution of the bromide in pyridine and dry ether is treated with hydrogen sulfide at -10°. A pure white precipitate is obtained which is fairly soluble in pyridine and ammonium sulfide. (SHg). It is insoluble in common solvents. When wet it is unstable, turning black in a few hours. Kept dry and dark in a vacuum it is stable for several days. It decomposes on heating without melting.

Mercury Derivatives of Aromatic Nitro Compounds.

o-Nitrophenylmercuric Chloride.[150]

Mercuric acetate is heated with five times its weight of nitrobenzene in an oil bath at 150° until it is all dissolved. The heating is continued until a sample gives no mercuric oxide when tested with sodium hydroxide. On cooling a small amount of a white crystalline substance separates. This gives the reactions of a mercurous compound but is not mercurous acetate. The filtrate from these crystals is treated with an excess of sodium chloride solution and steam distilled to remove the excess of nitrobenzene. The residue is dried, powdered, and extracted with 100-120° ligroin. Almost all of the solid dissolves. On cooling, fine slightly yellow crystals are obtained. These are re-

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[149] Kurssanov, *Chem. Zentr.* 1899 II 477.

[150] Dimroth, *Ber.* 35 (1902), 2036.

crystallized from glacial acetic acid. M.P. 182°. It is insoluble in water and most organic solvents but is soluble in ether and in high boiling ligroin. When treated with bromine it gives o-bromonitrobenzene.

o-Nitrophenylmercuric chloride does not react with arsenic trichloride either on the water bath or at 200°.[151]

This substance has also been made by the method of Peters from o-nitrobenzene sulfinic acid and mercuric chloride in aqueous alcohol.[151a] The reaction is complete in 45 minutes. The precipitate is extracted with hot acetone. The extract is evaporated to dryness and the residue is crystallized from alcohol. It forms faintly yellow crystals which melt at 185° (corr.). Yield 78 per cent. (N). It is very soluble in acetone, soluble in hot alcohol, very little soluble cold. It does not react with ammonium sulfide. Boiling hydrochloric acid gives nitrobenzene. Bromine in potassium bromide solution gives o-bromonitrobenzene. Boiling for hours with an excess of 5 per cent sodium hydroxide gives no action.

The identity of the compounds obtained directly from nitrobenzene and from o-nitrobenzene sulfinic acid prove that the direct mercuration of nitrobenzene introduces the mercuri group in the ortho position.

m-Nitrophenylmercuric Chloride.[152]

m-Nitrobenzene sulfinic acid and mercuric chloride are boiled in aqueous alcohol for 20 hours. The product is isolated in the same way as the ortho compound. Yield 42 per cent. M.P. 236-7° (corr.) (NHg). It is less soluble than the ortho compound. It reacts less readily with hydrochloric acid than the ortho and para compounds. Bromine converts it to m-bromonitrobenzene.

p-Nitrophenylmercuric Chloride.[153]

It is prepared from the sulfinic acid in the same way as the ortho and meta compounds. It separates from alcohol in colorless needles which melt with decomposition at 265-6° (corr.) (N). Its properties and solubilities resemble those of the ortho compound. Bromine transforms it to p-bromonitrobenzene.

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[151] Roeder and Blasi, Ber. 47 (1914), 2752.

[151a] Kharasch and Chalkley, *J. Am. Chem. Soc.* 43 (1921), 611.

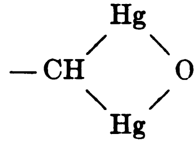
[152] *Ibid.*

[153] *Ibid.*

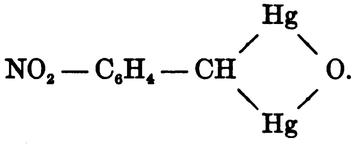
Mercuribis-2, 4, 6-trinitrobenzene.[154]

The mercuric salt of trinitrobenzoic acid on heating loses two molecules of carbon dioxide and forms the mercury diphenyl derivative.

As would be expected, the bromonitrobenzenes do not give organic mercury compounds when treated with sodium amalgam.[155]

The *nitrotoluenes* react with hot sodium hydroxide and mercuric oxide to form compounds in which the mercury enters the methyl group. The ortho compound gives mainly a disubstituted product containing the grouping  $-\mathrm{CH}\langle{}^{\mathrm{Hg}}_{\mathrm{Hg}}\rangle\mathrm{O}$. A smaller amount of a monosubstituted product is obtained having the grouping $-\mathrm{CH_2}-\mathrm{HgOH}$. The para compound and the dinitro compound give mixtures which are hard to separate.[156]

Anhydride of o-nitrobenzal dimercuric hydroxide,



$$\mathrm{NO_2}-\mathrm{C_6H_4}-\mathrm{CH}\langle{}^{\mathrm{Hg}}_{\mathrm{Hg}}\rangle\mathrm{O}.$$

Preparation.

Mercuric oxide, prepared from cold mercuric chloride solution and cold sodium hydroxide, is well washed and mixed with dilute sodium hydroxide solution. The mixture is heated to boiling under a reflux condenser. It is stirred by a current of air. The o-nitrotoluene is added gradually in small amounts. The mixture is boiled for one and a half hours and then cooled. The precipitate is filtered off and dried. Yield 96 per cent. (CHNHg). The mother liquor treated with dilute hydrochloric acid gives a precipitate of the impure monosubstituted compound, $\mathrm{NO_2}-\mathrm{C_6H_4}-\mathrm{CH_2}-\mathrm{HgCl}$.

Properties.

The anhydride forms an intensely yellow solid. It is insoluble in common solvents but is fairly soluble in acetic acid and less so in 20

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[154] Private communication, M. S. Kharasch.

[155] Dreher and Otto, *Ann.* 154 (1870), 125.

[156] Reissert, *Ber.* 40 (1907), 4209.

per cent sulfuric acid. It is soluble, even in the cold, in sodium bisulfite solution. This solution decomposes on standing.

The best method of purifying the anhydride is to dissolve it in a large volume of hot 20 per cent acetic acid. On cooling and diluting, a slight precipitate forms. This is filtered off and the filtrate is treated with sodium hydroxide. At first, a light yellow precipitate of the acetate forms. On standing in contact with an excess of base this takes on the darker hue of the anhydride. The final product consists of deep yellow crystals which can be dried on the water bath without decomposition. It darkens and decomposes above 220°.

Reactions.

1. With acids.

The anhydride treated with hydrochloric acid of over 30 per cent is split, giving inorganic mercury and anthranil. This change makes possible a very interesting intramolecular oxidation and reduction. It is possible to go from o-nitrotoluene to the mercury compound, then to anthranil, and finally to anthranilic acid without the use of any oxidizing or reducing agent.

When the anhydride is rubbed with 10 per cent hydrochloric acid it is changed to *o-nitrobenzal dimercuric chloride,*

$$NO_2 - C_6H_4 - CH(HgCl)_2. \quad (NClH).$$

Treatment with sodium nitrite and sulfuric acid changes the anhydride to a *dinitrite* which reacts with 20 per cent hydrochloric acid giving o-nitrobenzaldehyde and an equal amount of its oxime. Total yield 73 per cent.

The anhydride treated with nitric acid gives o-nitrobenzaldehyde in 87 per cent yield and about 10 per cent of another product which is possibly o, o′ -dinitrotolane.

2. With halogens.

Treatment of the anhydride with the free halogens gives the three o-nitrobenzal halides.

3. With reducing agents.

Zinc dust and sulfuric acid reduce the anhydride to o-toluidine.

4. With sulfides.

A suspension of the anhydride treated with hydrogen sulfide for five hours changes only partially to o-nitrotoluene and mercuric sulfide. About 80 per cent of the material remains unchanged.

Besides the dichloride and the dinitrite mentioned above a *basic chloride* and a *basic sulfate* have been prepared from the anhydride. A normal *nitrate* and *sulfate* have also been prepared.

o-Nitrobenzylmercuric chloride, $NO_2 — C_6H_4 — CH_2 — HgCl$.

If the mother liquors from the disubstituted compound are treated with an excess of dilute hydrochloric acid a small amount of the monosubstituted compound is precipitated. This can be purified by treating with sodium hydroxide, filtering, and acidifying with hydrochloric acid and then repeating the process, using ammonium hydroxide instead of sodium hydroxide. This process gives colorless crystals. (CHNClHg). M.P. 145-6°. It is easily soluble in acetone and benzene, less soluble in alcohol, rather difficultly in ether, and very little in water. It is soluble in bases.

p-Nitrotoluene treated with sodium hydroxide and mercuric oxide gives no alkali soluble product. The insoluble product obtained contains more than two atoms of mercury. An excess of dilute nitric acid gives p-nitrobenzoic acid indicating that the mercuration takes place in the side chain.

2, 4-Dinitrotoluene reacts very readily with mercuric oxide and sodium hydroxide or sodium ethylate. The products are hard to purify. They react more readily with sulfides than do the mercury compounds of o-nitrotoluene. Treatment with nitric acid of Sp. g. 1.4 gives 2, 4-dinitrobenzoic acid.

Mercury di-(2, 4-dinitrobenzyl).[157]

The mercuric salt of 2, 4-dinitrophenyl acetic acid is heated to eliminate two molecules of carbon dioxide. If the product is heated still hotter it loses metallic mercury and forms tetranitrodibenzyl. This loss of mercury takes place more rapidly in the presence of pyridine.

Mercury Derivatives of Sulfinic and Sulfonic Acids.

Benzene sulfinic acid and *p-toluene sulfinic acid* react with mercuric chloride at 0° to form mercuric salts of the acids. If heated with alcoholic mercuric chloride the sulfinic acids give sulfur dioxide, hydrochloric acid, and the corresponding arylmercuric chloride. There is also some reduction of the mercuric chloride to calomel. If the ace-

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[157] Private communication, M. S. Kharasch.

tate or nitrate is used instead of mercuric chloride much metallic mercury is formed.[158]

This method has recently been applied in the preparation of the three nitrophenylmercuric chlorides from the corresponding nitrosulfinic acids.[159] It has also been applied in the preparation of beta-naphthylmercuric chloride.[160]

Benzene sulfonic acid can be mercurated by heating with mercuric oxide until the solution gives no action with sodium hydroxide. The product has not been obtained pure. Treatment of the impure substance with bromine gives m-bromobenzoic acid and some dibromobenzoic acid. These results indicate that the mercury enters the nucleus in the *meta* position to the sulfonic acid group. If this is true the case is of great interest as being the only one in which mercury takes a position meta to the orienting group. The mercuration of benzoic acid and nitrobenzene give ortho compounds.[161]

Mercury Derivatives of Phenylacetylene.

Phenylacetylene when treated with mercuric salts gives products which on acidification yield acetophenone. This reaction resembles that of acetylene which gives acetaldehyde. In each case the net result is the addition of water to the triple bond. As in the case of acetylene, there is no agreement as to the mechanism of the reaction. Manchot[162] believes that the mercury compound is a complex molecular compound of mercuric phenyl acetylide and mercuric salts while Biltz[163] regards this compound as acetophenone mercurated in the methyl group. The former believes that acidification simply liberates phenylacetylene which is then hydrated more rapidly in the presence of the mercuric salts which are formed in the reaction. The latter believes that the mercurated acetophenone gives the usual reaction of organic mercury compounds with acids, namely, the replacement of mercury by hydrogen. Manchot strengthens his argument by showing that the triple bond can be hydrated by acid alone. Thus phenyl acetylene gives a small amount of acetophenone when heated with

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[158] Peters, *Ber.* 38 (1905), 2567.

[159] Kharasch and Chalkley, *J. Am. Chem. Soc.* 43 (1921), 611.

[160] Unpublished results, Whitmore and L. F. Howe.

[161] Reissert, loc. cit. Dimroth, *Chem. Zentr.* 1901 I 450. Rother, *Dissert.* Berlin 1911, p. 8.

[162] Manchot and Haas, *Ann.* 399 (1913), 123.

[163] Biltz and Reinkober, *Ann.* 404 (1914), 219.

dilute hydrochloric acid. Piperonylacetylene boiled with hydrochloric acid even for a few minutes is changed completely to the ketone.[164]

Phenyl acetylene treated with mercuric chloride gives an oil unless an excess of the mercuric salt is used. In that case crystals are obtained. These crystals give analyses for $C_{16}H_{11}Hg_5Cl_5O_2$ or $C_{16}H_{13}Hg_5Cl_5O_3$. Manchot gives molecular formulas corresponding to these empirical formulas:—

I. $(C_6H_5C \equiv C)_2Hg.2HgCl_2.HgO.Hg(OH)Cl$.
II. $(C_6H_5C \equiv CH)_2.2HgCl_2.2HgO.Hg(OH)Cl$.

The first seems more probable. When two molecules of phenyl acetylene react with an excess of mercuric chloride almost exactly 5 molecules of hydrochloric acid are split out as can be shown by titrating the filtrate from the mercury compound. The formation of the compound $C_6H_5 — CO — C(HgCl)_3$ would require the formation of 6 molecules of hydrochloric acid instead of 5. Biltz believes that Manchot's result of about 5 molecules of hydrochloric acid can be explained in the following ways:

1. The experimental difference is not great.
2. The product may contain some dimercurated product the formation of which would give a smaller amount of acid.
3. Some of the phenyl acetylene may have remained unchanged. It would be more logical to do the calculations from the amount of precipitate actually formed than from the amount of material exposed to the reaction.[165]

Mercuric phenylacetylide [166] reacts with mercuric chloride and a little hydrochloric acid giving the same product as phenyl acetylene itself. This method of preparation throws no light on the nature of the product as the acid used may liberate phenyl acetylene which then reacts with the mercuric salt.

Properties of the product from phenyl acetylene and mercuric chloride.

It forms a white amorphous solid insoluble in all common solvents. It gives no reaction with bases. Ammonium sulfide blackens it at once with the formation of mercuric sulfide. Four samples of the substance made with amounts of mercuric chloride varying from 1.8 to 3 molecules give analyses as follows: 6 analyses for carbon, 13.28 to 13.78;

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[164] Manchot and Haas, loc. cit.
[165] Biltz and Reinkober, loc. cit.
[166] Nef, *Ann.* 308 (1899), 299.

6 for hydrogen, .91 to 1.42; 11 for mercury, 69.72 to 72.39; 2 for chlorine, 12.91 and 12.97.

Reactions.

1. Action with hydrochloric acid.

If the precipitate is refluxed with dilute hydrochloric acid and not steam distilled for several hours the only product is acetophenone. The precipitate from 8 gm. of phenyl acetylene gives 6.4 gm. of acetophenone and no phenyl acetylene. However, if the mixture is steam distilled as soon as the acid is added a little phenyl acetylene is formed. In this way 35 gm. of the precipitate yields .9 gm. of phenyl acetylene boiling over a range of 27 degrees and 4.1 gm. of acetophenone boiling over a range of 5 degrees. If all of the precipitate were changed to phenylacetylene it would give 5. gm. If acetophenone were the only product the yield would be 5.9 gm.

2. Action with bromine.

The precipitate suspended in chloroform reacts with four atoms of bromine for every triple bond originally present. No hydrobromic acid is formed. If more bromine is added it acts more slowly and hydrobromic acid escapes. The organic products of these reactions have not been studied. Manchot suggests that the reaction with four atoms of bromine gives mercuric bromide and phenylacetylene dibromide. A more natural product would appear to be tribromostyrene, $C_6H_5 — CBr = CBr_2$. If Biltz is right in assuming that the precipitate is a mixture of di- and tri-mercurated acetophenones the product of bromination should be a mixture of di- and tribromacetophenones. A careful study of the organic product of the bromination might well throw light on the true nature of the original precipitate.

Product of the action of phenyl acetylene with mercuric bromide.[167]

Phenyl acetylene treated with 3 molecules of mercuric bromide in a large volume of water yields a crystalline yellowish precipitate. This is insoluble in water and only very slightly soluble in organic solvents. Long extraction with solvents produces no change in the composition. The analyses for carbon, hydrogen, mercury, and bromine agree fairly well with the formulas $C_{16}H_{10}Hg_4Br_4O$ and $C_8H_6Hg_2Br_2O$. Manchot uses the following molecular formulas:

I. $(C_6H_5C \equiv C)_2Hg.2HgBr_2.HgO$.

II. $C_6H_5C \equiv CH.HgBr_2.HgO$.

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[167] Manchot and Haas, loc. cit. 144.

Again the first formula is the more likely. The substance does not react with bases even on heating. With ammonium sulfide it gives mercuric sulfide at once.

Reactions.

1. With hydrochloric acid.

Refluxing with dilute acid gives no change. Concentrated hydrochloric acid gives an oil. If this is steam distilled at once it yields 1.9 gm. of phenylacetylene boiling over a range of 7 degrees and 1.4 gm. of acetophenone of M.P. 17-18°. The theoretical yield would be 5.3 gm. or 6.3 gm. respectively.

2. With bromine.

As in the case of the compound from mercuric chloride 4 bromine atoms react for every triple bond used. The organic product has not been studied.

Mercuric phenylacetylide, $(C_6H_5 — C \equiv C)_2Hg.$[168]

Phenylacetylene and mercuric oxide give a product which can be recrystallized from hot alcohol in white leaflets. Treatment with mercuric chloride and a little hydrochloric acid gives the same product as phenyl acetylene itself. It is easily soluble in ether. Manchot extracted the precipitates obtained from phenyl acetylene and mercuric salts with ether but was unable to remove any of the acetylide assumed to be present in the "molecular" compounds. He concluded that the acetylide must be "chemically combined" in the compounds.

Mercury Derivatives of Naphthalene.

α-Mercury Dinaphthyl.

Preparation.

Alpha bromonaphthalene heated with xylene and pasty sodium amalgam for 18 hours on an oil bath gives small yellowish crystals of the mercury compound.[169] A better yield is obtained if benzene is used as the solvent and one-tenth volume of ethyl acetate is added.[170] Four per cent sodium amalgam is recommended.[171]

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[168] Nef, loc. cit.

[169] Otto and Mörles, *Ann.* 147 (1868), 167.

[170] Otto, *Ann.* 154 (1870), 188.

[171] Michaelis, *Ber.* 27 (1894), 249.

Properties.

Alpha mercury dinaphthyl forms small white shiny rhombic prisms. It is odorless and is unchanged by air or light. It is insoluble in water, slightly soluble in boiling alcohol, cold benzene, and ether, easily soluble in hot carbon disulfide and chloroform, less easily soluble in boiling benzene. Alcohol or ether will precipitate it from its solution in carbon disulfide. It is best crystallized from hot benzene, carbon disulfide, or amyl alcohol. (CHHg). M.P. 243°. On heating to a higher temperature it gives carbon, mercury, and a brown oil which crystallizes on cooling. The density of alpha mercury dinaphthyl is about 1.9.[172]

Reactions.

1. Heating.

When mercury dinaphthyl is heated with soda lime the products are mercury, naphthalene, and a substance melting at 133° which may be impure $\alpha\alpha'$-dinaphthyl (M.P. 154°).[173]

2. With metals.

A solution in carbon disulfide does not react with zinc, copper, or tin in the cold. No experiments at higher temperatures have been tried.

3. With halogens.

Iodine in carbon disulfide gives a compound which was at first thought to be $(C_{10}H_7)_2HgI_2$ but has since been found to be alpha naphthylmercuric iodide. An excess of iodine gives mercuric iodide. The other product in these reactions is α-iodonaphthalene which was first made by this process. Bromine acts like iodine.

4. With acids.

Hydrochloric acid gives mercuric chloride and naphthalene. No mention is made of any intermediate formation of naphthylmercuric chloride. Formic acid gives naphthylmercuric formate and naphthalene. Similar reactions are obtained with acetic and butyric acids. Fuming nitric acid acts violently even in the cold giving mercuric nitrate and nitro derivatives of naphthalene. Dilute nitric acid gives some unnitrated naphthalene. Concentrated sulfuric acid gives mercuric sulfate and naphthalene sulfonic acid. 15 per cent hydrocyanic

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[172] Schröder, *Ber.* 12 (1879), 564.

[173] Otto and Möries, loc. cit.

acid gives no action even on heating. The filtrate contains no mercuric ions.[174]

5. With arsenic trichloride.[175]

The products of the reaction at a high temperature are mercuric chloride and α-naphthyl dichlorarsine.

6. With thionyl chloride.

A stormy reaction results when thionyl chloride is added to α-mercury dinaphthyl. The mixture must be cooled. When water is added an oil separates. When this is washed with water and ether it solidifies. The solid can be distilled, most of it boiling at 256°. The distillate solidifies and can be recrystallized from alcohol, M.P. 60° corresponding to beta chloronaphthalene. Apparently this change of an alpha to a beta derivative of naphthalene has not been questioned or studied farther.[176]

7. With mercuric salts.

Mercuric chloride in acetone reacts readily to form α-naphthylmercuric chloride.[177] 1 gm. of α-mercury dinaphthyl is added to 50 c.c. of hot acetone which is insufficient to dissolve it. When .6 gm. of mercuric chloride is added all goes into solution. Cooling causes the separation of 1.4 gm. of α-naphthylmercuric chloride. The same reaction carried out in carbon disulfide solution appears to give entirely different results. Mercury dinaphthyl warmed a long time with mercuric chloride in carbon disulfide and then evaporated, leaves a residue from which water extracts mercuric chloride leaving unchanged mercury dinaphthyl.[178] Mercury dinaphthyl heated one hour with mercuric iodide and alcohol at 150° gives α-naphthylmercuric iodide.[179]

8. With oxides of nitrogen.

Nitrogen trioxide in chloroform at 0° gives α-naphthyl diazonium nitrate and a solution of α-naphthylmercuric nitrate. This cannot be isolated but gives a precipitate of the chloride when treated with dilute hydrochloric acid. Nitrogen textroxide in chloroform at 0° gives a bright yellow crystalline precipitate which is soluble in alcohol. If treated with dilute hydrochloric acid it gives α-naphthyl mer-

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[174] Otto and Möries, loc. cit.

[175] Kelbe, *Ber.* 11 (1878), 1503. Michaelis and Schulte, *Ber.* 15 (1882), 1954.

[176] Heumann and Köchlin, *Ber.* 16 (1883), 1627.

[177] Steinkopf, *Ann.* 413 (1917), 313, 330.

[178] Otto and Möries, loc. cit.

[179] Otto, *Ann.* 154 (1870), 190.

curic chloride. The filtrate from the original precipitate gives naphthalene. No diazonium nitrate or nitroso compound is formed.[180]

9. Miscellaneous.

An alcohol solution of α-mercury dinaphthyl does not react with hydrogen sulfide. Sodium amalgam and alcohol give no action on the mercury compound. Ethyl iodide gives no action.

α-Naphthylmercuric chloride.

Preparation.

1. From mercury dinaphthyl and mercuric chloride in alcohol or acetone.
2. From the nitrate and dilute hydrochloric acid.

Properties.

It forms silky quadratic tablets. It is insoluble in water, difficultly soluble in hot alcohol, more soluble in hot benzene. M.P. 188-9°. It reacts with sodium iodide in acetone giving α-naphthylmercuric iodide but no mercury dinaphthyl.[181]

α-Naphthylmercuric bromide.

Preparation.

1. From mercury dinaphthyl and bromine.
2. From mercury dinaphthyl heated with mercuric bromide and alcohol one hour at 120°.
3. From naphthyl magnesium bromide and mercuric bromide heated.[182]

Properties.

The bromide forms shiny pointed leaflets. M.P. 202°. It is very soluble in aniline from which it separates in well formed crystals. It can also be recrystallized from pyridine. It is insoluble in water, soluble in hot alcohol, chloroform, benzene, and carbon disulfide.

Reactions.

An excess of ethyl magnesium bromide gives mercury diethyl.[183] An excess of α-naphthyl magnesium bromide gives only a small yield of α-mercury dinaphthyl.[184]

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[180] Kunz, *Ber.* 31 (1898), 1531.

[181] Steinkopf, loc. cit.

[182] Hilpert and Grüttner, *Ber.* 46 (1913), 1686.

[183] Hilpert and Grüttner, *Ber.* 48 (1915), 908.

[184] Hilpert and Grüttner, *Ber.* 46 (1913), 1686.

α-Naphthylmercuric iodide.

Mercury dinaphthyl is treated with iodine in carbon disulfide or is heated with mercuric iodide and alcohol at 150°. The iodide is insoluble in ether and water, soluble in hot alcohol, chloroform, benzene, and carbon disulfide. It is best crystallized from a large volume of boiling alcohol or a mixture of alcohol and benzene. (I). M.P. 185°. It reacts with sodium amalgam in alcohol or benzene giving α-mercury dinaphthyl.[185]

α-Naphthylmercuric formate.

Mercury dinaphthyl is treated with formic acid and the resulting solution is poured into water. The formate is an oil.[186]

α-Naphthylmercuric acetate.

Preparation and *Properties.*

Mercury dinaphthyl is dissolved in glacial acetic acid and the solution is diluted with water. The naphthalene is filtered off and the filtrate is evaporated to obtain the acetate. The acetate is easily soluble in hot alcohol from which it separates in fine needles on cooling. It is almost insoluble in water, slightly soluble in ether, easily soluble in hot acetic acid, alcohol, carbon disulfide, benzene, and chloroform. It is soluble in fats.[187] M.P. 154°.

Reactions.

1. Heating above the melting point gives carbon and an oily distillate.
2. With hydrochloric acid it gives naphthalene, mercuric chloride, and acetic acid.
3. With sodium amalgam.

In alcohol the reaction gives naphthalene, sodium acetate, and metallic mercury. This is in distinct contrast to the action of the iodide which gives α-mercury dinaphthyl when treated with sodium amalgam even in alcohol.

4. With sulfides.

An alcoholic solution reacts with hydrogen sulfide giving a white cheesy precipitate which is insoluble in common solvents except benzene which dissolves it slightly. Heating with an excess of ammonium

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[185] Otto, *Ann.* 154 (1870), 190.

[186] *Ibid.*

[187] Fraenkel, *Arzneimittelsynthese*, 4th Ed. 1919, 671.

sulfide at 100° gives naphthalene, ammonium acetate, and mercuric sulfide.

5. With halogens.

Iodine gives mercuric iodide, acetic acid, and naphthyl iodide.

α-Naphthylmercuric butyrate.

Mercury dinaphthyl is treated with butyric acid. The product consists of fine silky rhombic needles. M.P. 200°. It is hardly soluble in cold water, readily soluble in hot water, alcohol, and butyric acid.

α-Naphthylmercuric thiocyanate.

Mercury dinaphthyl and mercuric thiocyanate are heated in alcohol at 120°. The product forms fine white tablets which are soluble in hot alcohol and benzene.[188]

α-Naphthylmercuric nitrate.

The chloride is treated with alcoholic silver nitrate. The nitrate is also obtained in chloroform solution by treating mercury dinaphthyl with nitrogen trioxide. It forms fine white needle crystals. It reacts with dilute hydrochloric acid giving the chloride.

α-Naphthylmercuric sulfide.

The acetate is treated with ammonium sulfide. The sulfide is a cheesy white precipitate. It is slightly soluble in benzene. It reacts with an excess of ammonium sulfide at 100° to form mercuric sulfide, naphthalene, and ammonium acetate.

β-Mercury Dinaphthyl.

Preparation.

β-Bromonaphthalene mixed with three volumes of dry xylene and 5 per cent ethyl acetate is refluxed for 30 hours with a large excess of sodium amalgam which is just liquid at room temperature. An excess of benzene is added, the mixture is heated, and filtered hot. A white crystalline product is obtained in a yield of about 30 per cent. The product is recrystallized from benzene. β-Chloronaphthalene reacts with sodium amalgam but gives a much poorer yield of the mercury compound.[189]

Properties.

β-Mercury dinaphthyl forms white glistening scales or flat needles.

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[188] Otto, *J. prakt. Chem.* (2) 1 (1870), 182.

[189] Chattaway, *J. Chem. Soc.* 65 (1894), 878. Michaelis, *Ber.* 27 (1894), 251.

M.P. 238°. It is insoluble in ether and alcohol, moderately soluble in hot benzene and its homologs, chloroform, ethylene dibromide, and carbon disulfide.

Reactions.

1. With mineral salts. Mercuric salts and naphthalene or substituted naphthalenes are obtained.
2. Distillation over red hot soda lime gives ββ′-dinaphthyl and other products.
3. With arsenic trichloride.[190]

The reaction takes place as usual giving mercuric chloride and the naphthyl dichlorarsine.

β-Naphthylmercuric halides.

The halides have been prepared from β-mercury dinaphthyl. The *chloride* and *bromide* form colorless needles while the *iodide* forms slightly yellow leaflets. The chloride is the most soluble of the three although it is difficultly soluble in all organic solvents except hot amyl alcohol. The melting points are as follows: chloride 271°, bromide 266°, iodide 251°.

β-Naphthylmercuric chloride can be more conveniently prepared by the method of Peters from the sulfinic acid and mercuric chloride.[191]

β-Naphthylmercuric formate.

The mercury dinaphthyl is heated a long time with pure formic acid and the solution is precipitated by water. After drying, the naphthalene is removed by low boiling ligroin. The residue is crystallized from alcohol. It forms fairly large colorless glassy leaflets which turn gray in light. It is easily soluble in alcohol, fairly soluble in ether, benzene, and chloroform, insoluble in water. M.P. 155-8°. The corresponding *acetate* is made in a similar way and has similar properties. M.P. 148°.

Mercury Compounds of Naphthalene Sulfonic Acids.[192]

When the sodium salt of α- or β-naphthalene sulfonic acid is heated with mercuric acetate a white substance is obtained which reacts with

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[190] Michaelis, *Ann.* 320 (1902), 342.

[191] Unpublished results, Whitmore and L. F. Howe.

[192] Brieger and Schulemann, *J. prakt. Chem.* (2) 89 (1914), 154.

sodium hydroxide like a mercuric salt. This white substance is dissolved in acetic acid and treated with sodium hydroxide until the precipitate barely clears on shaking. The solution is evaporated on the steam bath. White crystals are formed. These dissolve readily in water. In dilute solution the new substance acts like a mercuric salt toward sodium hydroxide. In concentrated solution the mercury is in some form which does not react with sodium hydroxide. If the concentrated solution is heated with sodium hydroxide mercuric oxide is obtained.

Mercury Derivative of Dihydronaphthalene.[193]

Dihydronaphthalene reacts with mercuric salts in such a way that the groups —HgX and —OH add to the double bond in the alicyclic ring. It thus resembles the simpler ethylene derivatives.

ac-2-Acetoxymercuri-3-hydroxy-tetrahydronaphthalene.

An ether solution of dihydronaphthalene is shaken for 24 hours with an aqueous solution of mercuric acetate. Long needles separate. These can be crystallized from benzene or ligroin. M.P. 122°. The substance is soluble in bases. (No analyses.) The corresponding *bromide* is obtained by dissolving the acetate in potassium hydroxide, adding the calculated amount of potassium bromide, and saturating with carbon dioxide. The precipitate is washed with water and crystallized from benzene. It forms white shining crystals. (CHHg). M.P. 159°. The *iodide* is prepared in the same way as the bromide and has similar properties. (CH). It melts at 156° turning red.

Mercury Derivatives of Biphenyl.[194]

Mercuribis-biphenyl, $(C_6H_5 — C_6H_4 —)_2Hg$.

The parabromide is treated with sodium amalgam in the usual way. The product separates from hot benzene in small scales. (CHHg). M.P. 216°. It is very difficultly soluble in common solvents. It is very stable, not being changed by prolonged boiling with concentrated hydrochloric acid. When heated in sealed tubes with mercuric halides and alcohol it gives the corresponding p-biphenyl-mercuric halides which are white crystalline powders melting above 325°.

Dimercuribis-biphenyl, $Hg(C_6H_4 — C_6H_4)_2Hg$.

The product from 4, 4′-dibromobiphenyl and sodium amalgam may have this structure. It is extremely insoluble. (No analyses.)

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[193] Sand and Genssler, *Ber.* 36 (1903), 3706.

[194] Michaelis, *Ber.* 28 (1895), 592.

Chapter X.

Mercury Compounds of Aromatic Amines.

Mercury Compounds of Aniline.

The compounds obtained from aniline and mercuric salts may be divided into three classes: I—Substances of a salt-like nature obtained by the direct union of molecules of the constituents. II—Compounds in which hydrogen of the amino group is replaced by mercury. III—Compounds in which hydrogen of the nucleus has been replaced by mercury.

Double Compounds of Aniline and Mercuric Salts.

Mercuric chloride compounds.

A compound of this type was noted as long ago as 1842.[1] Aniline and mercuric chloride in alcohol form a white crystalline compound. It appears to have the formula $(C_6H_5NH_2)_2(HgCl_2)_3$. (CClHg). Boiling water decomposes it giving aniline and a yellow compound which was not studied.

The most common aniline compound of this type is the white crystalline substance obtained from the alcoholic mother liquors from the action of aniline and mercuric chloride.[2] The substance has the composition $(C_6H_5NH_2)_2.HgCl_2$ and probably consists of one molecule of mercuric chloride added to two amino groups in much the same way that two molecules of hydrochloric acid would add. Another compound $C_6H_5NH_2.HgCl_2$ has been obtained.[3] A still different kind of compound has been obtained in acid solution, $C_6H_5NH_2.HCl.HgCl_2$.[4]

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[1] Zinin, *J. prakt. Chem.* (1) 27 (1842), 150. A. W. von Hofmann, *Ann.* 47 (1843), 62. *Ann. chim. phys.* (3) 9 (1843), 173.

[2] Schiff, *Compt. rend.* 56 (1863), 492. Forster, *Ber.* 7 (1874), 294. *Ann.* 175 (1875), 25. Gmelin, *Organische Chem.* 4th Ed. II 716. André, *Compt. rend.* 112 (1891), 996. Pesci, *Z. anorg. Chem.* 15 (1897), 215.

[3] Schiff, loc. cit. André, loc. cit.

[4] Swan, *Am. Chem. J.* 20 (1898), 618.

Many other double compounds of aniline are discussed in the Handbuch of Gmelin-Kraut-Friedheim-Peters.[5]

Mercuric bromide compounds.

The compound $(C_6H_5NH_2)_2.HgBr_2$ is made by heating the components together. It can be crystallized from alcohol. M.P. 110-12°. It is decomposed by boiling water.[6] Another mercuric bromide compound of aniline is known, $C_6H_5NH_2.HgBr_2$. M.P. 124°.[7]

Mercuric iodide compounds.

The compound $(C_6H_5NH_2)_2.HgI_2$, M.P. 60° (53°), may be crystallized from alcohol containing a trace of aniline. It is decomposed by pure alcohol giving mercuric iodide.[8] Another compound, $C_6H_5NH_2.HgI_2$ is obtained from mercuric iodide and a boiling alcoholic solution of aniline. It forms yellow crystals which are decomposed by hot alcohol. It is insoluble in water but easily soluble in aniline and in alcohol containing aniline.[9]

Mercuric nitrate compounds.[10]

Aniline poured into a mercuric nitrate solution gives a white precipitate to which is assigned the formula, "$N\left(\begin{matrix}C_6H_5\\HgH_2\end{matrix}\right)NO_3$." Boiling with water causes the loss of some aniline nitrate and the formation of a dense white crystalline powder, "$N\left(\begin{matrix}C_6H_5\\Hg_2H\end{matrix}\right)NO_3.5H_2O$." Boiling this substance for several days causes the elimination of more aniline nitrate with the formation of "$N\left(\begin{matrix}C_6H_5\\Hg_3\end{matrix}\right)NO_3.H_2O$." Boiling for eight days more gives no further change. The three compounds obtained react at once with sulfides but do not react with bases or iodides.

Mercuric nitrite compounds, $(C_6H_5NH_2)_2.Hg(NO_2)_2$.[11]

Mercuric cyanide compounds.

Aniline and hot aqueous mercuric cyanide give a crystalline product. This is unstable even at 80°. It gives no action with alkalies or

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[5] V-II 913-15.

[6] Klein, *Ber.* 13 (1880), 385. Staronka, *Chem. Zentr.* 1910 II 1743.

[7] Staronka, loc. cit.

[8] Klein, loc. cit. Staronka, loc. cit. François, *Compt. rend.* 121 (1895), 254, 768. *J. pharm. chim.* (6) 3 (1895), 49. *Chem. Zentr.* 1896 I 470.

[9] Vohl, *Arch. Pharm.* (2) 148 (1871), 201. *Jahresber.* 1871, 705. Schiff, *Compt. rend.* 56 (1863), 493.

[10] Schiff, *Compt. rend.* 56 (1863), 491.

[11] Ray, *J. Chem. Soc.* 101 (1912), 618.

iodides. It gives no color on heating, thus differing from most aniline mercuric salts.[12]

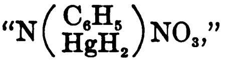
Mercuric sulfite compounds.

$C_6H_5NH_2.HgH_2(SO_3)_2.H_2O$ forms white lamellæ. (Hg,SO_2, Aniline).[13]

Mercuric chlorate and *perchlorate compounds* are amorphous precipitates.[14]

Mercuric acetate compounds.[15]

Mercurous nitrate compounds.

Aniline and mercurous nitrate form a white crystalline powder, "$N\left(\begin{matrix}C_6H_5\\HgH_2\end{matrix}\right)NO_3$," which gives metallic mercury readily on heating.[16]

Mercurous chloride does not act on aniline at 100°, at 150° it gives fuchsin.

N-Mercury Derivatives of Aniline.

While mercuric oxide will not react with aniline the latter will react with "nascent" mercuric oxide forming N-mercurianiline, $(C_6H_5NH—)_2Hg$.

N-Mercurianiline, $C_6H_5NH — Hg — NHC_6H_5$.[17]

Preparation and Properties.

A clear aqueous solution of pure aniline prepared from acetanilide is treated with small portions of sodium hydroxide and mercuric chloride. A crystalline powder is filtered off and washed with water containing a little aniline. The product is dried over sulfuric acid. It forms microscopic octahedra. It gives a strong alkaline reaction and has a strong caustic taste. It is decomposed by ordinary solvents. The only possible solvent is potassium hydroxide solution containing a small amount of aniline. Even this solvent cannot be used above 80° without decomposing the product.

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[12] Schiff, loc. cit. Staronka, loc. cit.

[13] Denigès, *Compt. rend.* 112 (1891), 805.

[14] Hofmann, *Ber.* 38 (1905), 2002.

[15] *Gmelin-Kraut-Friedheim-Peters Handbuch,* V-II 969.

[16] Schiff, loc. cit.

[17] Schiff, loc. cit. Pesci, *Gazz. chim. ital.* 22 I (1892), 373. *Z. anorg. Chem.* 15 (1897), 214.

Various formulas were assigned to this substance before the correct one was discovered.[18]

Reactions.

1. With acids.

Acids in excess form aniline salts and mercuric salts. A small amount of acid forms the compound in which mercury is substituted for hydrogen of the nucleus. This reaction probably consists in the removal of the mercury from the nitrogen forming a mercuric salt which then mercurates the nucleus.[19]

2. With mercuric salts.

Mercuric acetate reacts with N-mercurianiline forming p-aminophenylmercuric acetate. The mechanism of this reaction has not been studied.[20]

3. With sulfur compounds.

N-Mercurianiline reacts with carbon disulfide forming thiocarbanilide and mercuric sulfide. With thiourea it forms dicyandiamide, and with thiocarbanilide it forms triphenyl guanidine. The first two reactions run spontaneously at room temperature.[21]

"Phenylated White Precipitate."

Wislicenus before 1875 found that the treatment of alcoholic aniline with mercuric chloride gives not only the common soluble compound $(C_6H_5NH_2)_2.HgCl_2$, but also a yellowish white extremely insoluble compound of the composition C_6H_6NClHg. Forster made an exhaustive study of this substance and concluded that it is a phenyl derivative of infusible white precipitate, $NH_2 — HgCl$. It would thus have the structure, $C_6H_5NH — HgCl$ or possibly $C_6H_5N = Hg.HCl$.[22] Pesci came to the conclusion that Forster's compound was identical with the chloride obtained from the action of aniline and mercuric acetate followed by treatment with sodium chloride in the presence of

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[18] Pesci, *Atti accad. Lincei*, (5) I (1892), 312. *Gazz. chim. ital.* 22 I (1892), 373. *Chem. Zentr.* 1892 II 213. *Gazz. chim. ital.* 23 II (1893), 529; 27 I (1897), 568; 28 II (1898), 442. *Z. anorg. Chem.* 15 (1897), 213.

[19] Pesci, *Gazz. chim. ital.* 22 I (1892), 378; 27 I (1897), 569; 28 II (1898), 443.

[20] Pesci, *Gazz. chim. ital.* 27 I (1897), 567. *Chem. Zentr.* 1897 II 482.

[21] Pesci, *Gazz. chim. ital.* 27 I (1897), 572. *Chem. Zentr.* 1897 II 482. Montecchi, *Gazz. chim. ital.* 28 II (1898), 434. *Chem. Zentr.* 1899 I 381. Pesci, *Z. anorg. Chem.* 15 (1897), 214.

[22] Forster, *Ann.* 175 (1875), 29. *Ber.* 7 (1874), 294.

acetic acid. Pesci used an incorrect formula for this substance but Dimroth later showed that it is probably a polymer of the crystalline p-aminophenylmercuric chloride which is obtained in the absence of acetic acid.[23] The compound obtained by Pesci and by Dimroth undoubtedly has mercury attached to carbon but its identity with Forster's compound has by no means been proved.

"Phenylated white precipitate" is insoluble in all organic solvents. It is purified by exhaustive extraction with boiling alcohol. It may be identical with the yellow insoluble substance mentioned by Hofmann in 1843.[24]

Reactions.

An alcoholic solution of thiocarbanilide reacts slowly with "phenylated white precipitate" giving triphenyl guanidine. This reaction is used by Forster to prove that a phenylimido group is attached to mercury in the original substance. This proof loses some of its force when it is recalled that thiocarbanilide will react with substances like lead chloride giving triphenyl guanidine. Forster's line of reasoning applied to this case would "prove" that lead chloride contains a phenylimido group attached to lead. In spite of this apparent flaw Forster's reasoning may be correct as white precipitate itself reacts with thiocarbanilide forming diphenyl guanidine. A reaction which gives better support to the N — Hg structure is the action of "phenylated white precipitate" with monophenyl thiourea to form alpha-diphenyl guanidine.[25]

"Phenylated white precipitate" reacts with iodine forming iodaniline and diiodaniline.[26] This reaction has no value in settling the structure of the substance as the same products would be given by an N — Hg and a C — Hg compound.

André was unable to make a substance having the composition of Forster's phenylated white precipitate.[27] His analyses are C 16.3, H 1.47, Cl 15.0, Hg 64.4, N 2.64, figures which agree fairly well with a formula $(C_6H_5NH-HgCl)_5(HgCl_2)_2$. Long boiling of this gives a substance, $(C_6H_5NH-HgCl)_3.(HgCl_2)_2$.

Mercury acetamide and aniline hydrochloride in water solution

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[23] Pesci, *Z. anorg. Chem.* 15 (1897), 214. Dimroth, *Ber.* 35 (1902), 2037.

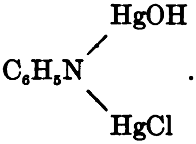
[24] A. W. von Hofmann, *Ann.* 47 (1843), 62.

[25] Forster, loc. cit. Byk, *J. prakt. Chem.* (2) 20 (1879), 335.

[26] Rudolph, *Ber.* 11 (1878), 78.

[27] *Compt. rend.* 112 (1891), 997.

give a yellow precipitate which is soluble in an excess of the hydrochloride solution. If enough of the hydrochloride is used a white crystalline precipitate of $(C_6H_5NH_2)_2.HgCl_2$ is formed. The yellow precipitate corresponds to the formula $C_6H_5NH — HgO — HgCl$.[28] Franklin suggests that this substance may have the structure,



$C_6H_5N\begin{array}{l}\diagup HgOH\\ \diagdown HgCl\end{array}$

.[29] Aniline itself reacts with mercury acetamide giving a viscous solid.[30]

True Organic Mercury Derivatives of Aniline.

p-Aminophenylmercuric Acetate.

Preparation.[31]

1. From N-mercurianiline and acetic acid.
2. From N-mercurianiline and a concentrated solution of aniline acetate.
3. From N-mercurianiline and mercuric acetate solution.
4. From aniline acetate and mercuric oxide.
5. *From aniline and mercuric acetate.*

One or two molecules of aniline can be used. Mercuric acetate dissolved in water is treated with freshly distilled aniline. On short standing thick, hard, slightly yellow prisms separate. After standing three hours these are filtered off. They consist of the practically pure para compound. On longer standing more of these prisms separate mixed with small crystals of the ortho compound. Yield 40 gm. of para compound and 3 gm. of ortho compound from 18.6 gm. of pure aniline treated with 31.8 gm. of mercuric acetate.

Properties.

p-Aminophenylmercuric acetate forms colorless thick prisms when pure. (CHHg). M.P. 167°. It is insoluble in water and ether, very

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[28] Fürth, *Monatsh.* 23 (1902), 1157.

[29] Franklin, *Am. Chem. J.* 47 (1912), 361.

[30] Forster, *J. Chem. Soc.* 73 (1898), 795. *Chem. News* 78 (1898), 250.

[31] Pesci, *Atti accad. Lincei* (5) 1 (1892), 312. *Gazz. chim. ital.* 22 I (1892), 373. *Chem. Zentr.* 1892 II 213. Piccinini and Ruspaggiari, *Gazz. chim. ital.* 22 II (1892), 604. Pesci, *Gazz. chim. ital.* 27 I (1897), 573. *Chem. Zentr.* 1897 II 482. Pesci, *Z. anorg. Chem.* 15 (1897), 215. Reitzenstein and Bönitsch, *J. prakt. Chem.* (2) 86 (1912), 76. Dimroth, *Ber.* 35 (1902), 2039.

difficultly soluble in alcohol and chloroform. It can be crystallized from the latter solvent. It has basic properties turning red methyl orange yellow. It is said to be readily soluble in dilute acids.[32] It is soluble in a water solution of aniline acetate. It is also soluble in dilute bases. Concentrated potassium hydroxide gives a compound of composition C_6H_5NHg.

Reactions.

1. With chlorides.

When the pure acetate is treated with aqueous sodium chloride solution, it is changed to a corresponding chloride which is crystalline and fairly soluble in the common organic solvents. If, however, the reaction is carried out in the presence of acetic acid by dissolving the acetate in acetic acid and then adding the chloride solution, an isomeric chloride is obtained which is amorphous and extremely insoluble in common solvents.[33] The amorphous chloride may be a polymer of the crystalline chloride. It was obtained in the same way by Pesci who did not obtain any of the crystalline form.[34] He believed it to be identical with the "phenylated white precipitate" obtained by Forster from boiling alcoholic solutions of aniline and mercuric chloride.[35]

2. With bromides.

Ammonium bromide gives p-aminophenylmercuric bromide. M.P. 182°.[36]

3. With iodides.

The acetate reacts with potassium iodide in such a way that a small amount of ionic mercury enters the solution. This has not been explained. The chief product is p-aminophenylmercuric iodide. M.P. 165°.

The following reactions involve the amino group without changing the acetoxymercuri group:

4. Acetylation.

Treatment with cold acetic anhydride gives *p-acetoxymercuriacetanilide,* $CH_3CONH — C_6H_4 — HgOAc$. The white powder can be recrystallized from hot water from which it separates in leaflets.

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[32] Jacobs and Heidelberger, *J. Biol. Chem.* 20 (1915), 515, find this statement of Dimroth to be untrue.

[33] Dimroth, *Ber.* 35 (1902), 2040.

[34] *Gazz. chim. ital.* 28 II (1898), 445.

[35] *Ann.* 175 (1875), 25.

[36] Piccinini, *Gazz. chim. ital.* 24 II (1894), 457. *Ber.* 28 R (1895), 113.

(CHHg). It softens at 220° and melts at 221°.[37] It is identical with the compound obtained from acetanilide and mercuric acetate.[38]

5. With aldehydes.

Salicylaldehyde in absolute alcohol reacts with the powdered acetate giving a mercurated Schiff's base,

$$AcOHg — C_6H_4 — N = CH — C_6H_4 — OH.$$

It forms deep yellow microcrystals, soluble in dilute sodium hydroxide, chloroform, and acetic acid. It is hydrolyzed with difficulty by boiling dilute hydrochloric acid. (NHg). On rapid heating it darkens at 140° and melts with decomposition at 185°.[39]

6. Diazotization and coupling.

p-Aminophenylmercuric acetate can be diazotized in the usual way. The solution of the diazonium salt gives coupling reactions with phenol, dimethylaniline, diethylaniline, resorcin, and alpha-naphthylamine-5-sulfonic acid. The mercurated azo dyes obtained in this way are rather insoluble substances of high melting or decomposition points. The alkaline solutions dye silk yellow or orange.[40]

7. With dinitrophenyl pyridine chloride.

The mercurated aniline reacts the same as aniline itself. The product is

$$AcOHg - C_6H_4 - N = (CH)_5 - NH_2Cl - C_6H_4 - HgOAc.$$

(CHN). M.P. 164°. It is insoluble in common solvents. If the reaction is carried out in boiling alcohol the dinitraniline formed reacts with one of the acetoxymercuri groups giving a product containing the linkage C — Hg — N which is probably

$$AcOHg - C_6H_4 - N = (CH)_5 - NH_2Cl - C_6H_4 - Hg\text{-}NH\text{-}C_6H_3(NO_2)_2.$$

(CHNHg). M.P. 244°. It is insoluble in all common solvents. The mother liquor gives a small amount of a substance which is said to be

$$AcOHg - C_6H_4 - N = (CH)_5 - NH_2Cl - C_6H_4 - HgOH.$$

(N). It blackens at 180° but does not melt at 250°. It seems highly improbable that the molecule of HCl would remain attached to the

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[37] Dimroth, *Ber.* 35 (1902), 2039.

[38] Pesci, *Gazz. chim. ital.* 24 II (1894), 449; 29 I (1899), 397.

[39] Jacobs and Heidelberger, *J. Biol. Chem.* 20 (1915), 518.

[40] *Ibid.*

second nitrogen in the formula instead of reacting with the strongly basic —HgOH group.[41]

8. With propargyl acetal.[42]

When the substances are boiled in alcohol for six hours the acetal odor disappears. When the yellow solution is acidified with dilute hydrochloric acid a light yellow powder is obtained. This blackens and decomposes at 180°. The analyses agree with no formula.

If the reaction is carried out in cold acetic acid a small amount of a yellow precipitate is obtained which gives a nitrogen analysis in agreement with the formula

$$AcOHg - C_6H_4 - NH - CH = CH - CH = N - C_6H_4 - HgOAc.HOAc.$$

p-Mercuribis-aniline, $(NH_2 - C_6H_4 -)_2Hg$.

Preparation.

1. p-Aminophenylmercuric acetate or hydroxide is treated with caustic alkali and then with sodium sulfide giving mercuric sulfide and the desired compound.[43]

2. Finely powdered p-aminophenylmercuric acetate is warmed with concentrated sodium thiosulfate solution until dissolved. A small amount of mercuric sulfide separates. This is quickly filtered off and the filtrate is cooled. White crystals separate. These are recrystallized from a little hot water. A little more mercuric sulfide separates. The crystals are sodium p-aminophenylmercuric thiosulfate, $NH_2 - C_6H_4 - HgS - SO_3Na$. (CHNaHg). M.P. 95° with decomposition. On standing, the substance turns brown and then black. When heated with water for some time it forms p-mercuribis-aniline.[44]

3. p-Aminophenylarsenious oxide, $NH_2 - C_6H_4 - AsO$, is heated with sodium hydroxide and mercuric chloride.[45]

4. p-Mercuribis-acetanilide $(CH_3CONH - C_6H_4 -)_2Hg$, is heated with alcoholic potassium hydroxide at 100°.[46]

Properties.

p-Mercuribis-aniline forms colorless needles soluble in chloroform, very little soluble in alcohol and benzene, insoluble in ether. M.P. 174° decomp.

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[41] Reitzenstein and Stamm, *J. prakt. Chem.* (2) 81 (1910), 151.
[42] Reitzenstein and Bönitsch, *J. prakt. Chem.* (2) 86 (1912), 77.
[43] Pesci, *Gazz. chim. ital.* 23 II (1893), 529; 28 II (1898), 446.
[44] Piccinini, loc. cit. Dimroth, *Ber.* 35 (1902), 2042.
[45] D. R. P. 272,289. Fränkel, *Arzneimittelsynthese,* 4th Ed. 1919, p. 661.
[46] Pesci, *Z. anorg. Chem.* 15 (1897), 223.

p-Aminophenylmercuric hydroxide and its anhydride, $H\overline{N—C_6H_4—H}g$ or $HN = C_6H_4 = Hg$.

Various formulas have been assigned to the basic substance obtained from p-aminophenylmercuric acetate and concentrated bases.

Preparation.

1. p-Aminophenylmercuric acetate dissolved in dilute potassium hydroxide and then treated with 30 per cent potassium hydroxide gives a precipitate of the hydroxide or its anhydride.[47]

2. A solution of mercuric nitrate added to an acid solution of aniline nitrate gives an immediate precipitate of white leaflets. Boiling water changes these to a compound which is soluble in dilute potassium hydroxide. When this solution is treated with concentrated potassium hydroxide a precipitate of the anhydride is obtained. (CHHg).[48]

Properties.

The anhydride forms colorless plates which become opaque on standing in air. It has a strong alkaline reaction and caustic taste. It is very little soluble in water, insoluble in ether. It combines readily with acids giving salts of p-aminophenylmercuri. It decomposes on heating.

Reactions.

1. With sulfides.[49]

The anhydride is suspended in water and treated with the calculated amount of sodium sulfide. After heating for some time the precipitate is filtered off and dried. It is then powdered and extracted with hot chloroform to remove the p-mercuribis-aniline. The residue is mercuric sulfide.

2. With methyl iodide and sulfides.[50]

The finely powdered anhydride is suspended in methyl alcohol and allowed to stand with methyl iodide in the cold for 24 hours. Then a little potassium hydroxide in methyl alcohol is added and the mixture is refluxed for a few hours. A yellow crystalline powder forms. This is treated with barium sulfhydrate giving a quarternary ammo-

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[47] Pesci, *Z. anorg. Chem.* 15 (1897), 214. Dimroth, *Ber.* 35 (1902), 2044.

[48] Piccinini and Ruspaggiari, *Gazz. chim. ital.* 22 II (1892), 609.

[49] Pesci, *Gazz. chim. ital.* 23 II (1893), 529. *Chem. Zentr.* 1894 I 501. *Ber.* 27 R (1894), 128.

[50] Pesci, loc. cit. Dimroth, *Ber.* 35 (1902), 2044.

nium compound of p-mercuribis-aniline. The changes involved may be indicated as follows:

$$(NH_2 - C_6H_4 - HgOH) \xrightarrow{CH_3I,\,KOH} I(CH_3)_3N - C_6H_4 - HgI$$

$$\xrightarrow{Ba(SH)_2} HgS + Hg[C_6H_4 - N(CH_3)_3I]_2$$

The product is the same as that obtained from p-mercuribis-dimethyl-aniline and methyl iodide.

p-Aminophenylmercuric chloride.

This substance exists in two forms, an amorphous insoluble form, and a crystalline form which is fairly soluble in organic solvents.

Preparation of the *amorphous* chloride.[51]

p-Aminophenylmercuric acetate dissolved in acetic acid is treated with sodium chloride solution.

Preparation of the *crystalline chloride.*[52]

The finely powdered acetate is boiled with a large volume of water containing a slight excess of sodium chloride. The hot solution is filtered. On cooling shining leaflets separate. These can be recrystallized from alcohol or benzene.

Properties of the amorphous form.

It is a pale yellow precipitate insoluble in all solvents, and dilute acids. (CHClHg). It is slightly soluble in potassium hydroxide. It is said to be identical with Forster's "phenylated white precipitate."

Properties of the crystalline chloride.

If forms shining leaflets which are soluble in hot alcohol and benzene. (CHNHg). M.P. 188°,[53] 240°.[54] The former is probably correct.

Reactions.

1. With aniline hydrochloride.[55]

The amorphous chloride dissolves in an alcoholic solution of aniline hydrochloride. On cooling it deposits crystals which decompose above 150° and are identical with Gerhardt's compound $(C_6H_5NH_2)_2.HgCl_2$.[56]

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[51] Pesci, *Z. anorg. Chem.* 15 (1897), 208. Dimroth, *Ber.* 35 (1902), 2041.

[52] Dimroth, loc. cit. Reitzenstein and Stamm, *J. prakt. Chem.* (2) 81 (1910), 156.

[53] Dimroth, loc. cit.

[54] Reitzenstein and Stamm, loc. cit.

[55] Pesci, loc. cit.

[56] *Chimie organique,* III 86.

The identity is proved by the fact that both compounds when boiled with water give the compound $(C_6H_5NHHgCl)_2.HgCl_2$. (CHNClHg).

2. With sodium thiosulfate.[57]

Both the amorphous and crystalline chlorides react with concentrated sodium thiosulfate giving sodium p-aminophenylmercuric thiosulfate which on heating gives p-mercuribis-aniline.

3. With dinitrophenyl pyridine chloride.[58]

The reaction in boiling alcohol gives a red brown powder to which is assigned the formula

$$ClHg\text{-}C_6H_4\text{-}N=CH\text{-}CH=CH\text{-}CH=CH\text{-}NH_2Cl\text{-}C_6H_4\text{-}HgOH.$$

(CHNClHg). M.P. 125°. It seems unlikely that the molecule of hydrochloric acid would react with the nitrogen forming a hydrochloride instead of reacting with the $—HgOH$ group forming $—HgCl$.

If the reaction is carried out in cold acetone solution, an unhydrolyzed product is obtained. This is a red brown powder melting at 151°. It is insoluble in common solvents. It is believed to have the formula

$$ClHg — C_6H_4 — N = (CH)_5 — NH_2Cl — C_6H_4 — HgCl.$$

(CHNClHg).

4. With propargyl acetal.[59]

When the substances are refluxed in benzene a light yellow precipitate is obtained which darkens at 160° and melts at 190°. No formula. If the reaction is carried out in a water suspension on the steam bath a yellow solid is obtained which sinters at 210° but gives no definite melting point. No formula is given for it.

5. With ethoxyacrolein acetal, $C_2H_5O — CH = CH — CH(OC_2H_5)_2$.[60]

The two substances are warmed on the water bath until no more alcohol is evolved. A dark brown liquid and a smeary precipitate are formed. The solid can be recrystallized from some of the acetal. It darkens at 160° and melts at 190°. Analyses for chlorine and mercury agree fairly well with the formula

$$ClHg — C_6H_4 — NH — CH = CH — CH(OC_2H_5)_2.$$

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[57] Dimroth, loc. cit.

[58] Reitzenstein and Stamm, loc. cit.

[59] Reitzenstein and Bönitsch, *J. prakt. Chem.* (2) 86 (1912), 78.

[60] *Ibid.*

p-Aminophenylmercuric bromide.

The acetate is dissolved in dilute acetic acid and treated with potassium bromide solution. The product is a slightly yellow precipitate which is amorphous and insoluble in water and common solvents. It is insoluble in acids but slightly soluble in bases. (Hg). M.P. 182°.

p-Aminophenylmercuric iodide.[61]

A solution of the acetate in acetic acid is precipitated by dilute potassium iodide solution. The product is amorphous and insoluble in water, common solvents, acids, and alkalies. (IHg). M.P. 165°.

Apparently no attempt has been made to secure the bromide or iodide in crystalline soluble forms corresponding to that obtained with the chloride when it is prepared in the absence of acetic acid.

p-Aminophenylmercuric nitrate.

The nitrate may be obtained directly from mercuric nitrate and a solution of aniline nitrate. It forms white leaflets.[62]

The nitrate can also be obtained from an acetic acid solution of the acetate treated with sodium nitrate solution. The white flakey crystals are insoluble in water but soluble in acids and bases. Boiling water changes it to a compound, "$C_6H_5NHg.HNO_3.C_6H_5NH_2.HNO_3$".[63]

p-Aminophenylmercuric acid sulfate.

The acetate suspended in water and treated with 50 per cent sulfuric acid gives a mass of colorless needle crystals which are insoluble in water, common solvents, acids, and bases. It decomposes at 150° without melting.

Sodium p-aminophenylmercuric thiosulfate,

$$NH_2 — C_6H_4 — HgS — SO_3Na.$$ [64]

The acetate is suspended in water and treated with warm concentrated sodium thiosulfate solution until all dissolves except a little mercuric sulfide. This is filtered off and the filtrate is cooled until colorless plates separate. These are quickly recrystallized from a small amount of water. M.P. 95° decomp. The substance turns brown

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[61] Pesci, loc. cit. and *Z. anorg. Chem.* 32 (1902), 231. Piccinini, loc. cit. Dimroth, loc. cit. and *Z. anorg. Chem.* 33 (1903), 314. Brieger and Schulemann, *J. prakt. Chem.* (2) 89 (1914), 104.

[62] Piccinini and Ruspaggiari, loc. cit.

[63] Pesci, *Gazz. chim. ital.* 22 I (1892), 380.

[64] Dimroth, *Ber.* 35 (1902), 2042.

or black on standing due to the separation of mercuric sulfide. The other product of the decomposition is p-mercuribis-aniline. The same change can be brought about more rapidly by heating the thiosulfate with water. The thiosulfate can also be made from the amorphous and crystalline p-aminophenylmercuric chlorides. (CHNaHg).

o-Aminophenylmercuric acetate.[65]

A small amount of the ortho compound is obtained from the mother liquor from the para compound. In properties, it resembles the para compound closely but is more soluble. It forms pearly leaflets from dilute alcohol. (CHN). M.P. 158-60°.

Reactions.

1. With sodium chloride.

Only one o-aminophenylmercuric chloride is obtained. It is crystalline and fairly soluble. This result is in sharp contrast to that obtained with the para compound which occurs in two forms.

2. Acetylation.

Cold acetic anhydride gives a clear solution. Crystals of *o-acetoxymercuri acetanilide* are obtained. M.P. 156-8°. This substance reacts with bromine giving o-bromacetanilide melting at 99° (Br). This proves the position of the mercury in the nucleus.

3. With dinitrophenyl pyridine chloride.

Short heating of the substances in acetone gives a red precipitate which gives a nitrogen analysis in agreement with the formula

$$AcOHg{-}C_6H_4{-}N{=}(CH)_5{-}NH_2Cl{-}C_6H_4{-}Hg{-}NH{-}C_6H_3(NO_2)_2.$$

o-Aminophenylmercuric chloride.

The mother liquor, from the preparation of p-aminophenylmercuric acetate from aniline and mercuric acetate, is treated with sodium chloride solution to form a mixture of the insoluble amorphous parachloride and the orthochloride which is soluble in hot alcohol. The amorphous p-chloride remains after the extraction with alcohol. The orthochloride forms long colorless plates from alcohol or acetic acid. (CHHg).

2-Amino-5-nitrosophenylmercuric chloride.[65a]

The corresponding mercurated p-nitrosophenol is warmed for half an hour on the water bath with ammonium chloride, acetate, and car-

[65] Dimroth, loc. cit. Reitzenstein and Bönitsch, *J. prakt. Chem.* (2) 86 (1912), 76.

[65a] Kharasch and Piccard, *J. A. C. S.* 42 (1920), 1855.

bonate. A slight brown precipitate is formed. This is dried in vacuo and crystallized from anisole. It is slightly soluble in benzene, gives a green solution in ether, and a reddish yellow solution in alcohol. (NClHg).

2, 4-Diacetoxymercuri aniline, $(AcOHg)_2C_6H_3-NH_2$.[66]

Preparation.

Aniline is treated with two molecules of mercuric acetate in aqueous solution. After standing two days white crystals begin to separate. These are purified by suspending in water, adding ammonium acetate, and then ammonium hydroxide to dissolve the crystals. After filtering, the solution is treated with acetic acid until practically neutral and then set aside for 12 hours. The white precipitate is extracted with hot water slightly acid with acetic acid. The ammonium hydroxide purification is repeated.

Properties.

The dimercurated aniline forms white crystals. (CHNHg). M.P. 206°. It is soluble in acetic acid, very little in hot water, and insoluble in alcohol. It dissolves in ammonium hydroxide, probably forming a compound of some kind.

Reactions.

Refluxing the acetate with acetic anhydride for 12 hours, adding water, and cooling gives white crystals of *2, 4-diacetoxymercuriacetanilide.*[67] This can be purified by dissolving in ammonium acetate and ammonium hydroxide and then precipitating by acetic acid. (Hg). When the dimercurated acetanilide is treated with bromine in acetic acid the product is 2, 4-dibromacetanilide melting at 146°.

When the diacetate is dissolved in a large amount of water and treated with dilute sodium hydroxide a white substance slowly separates. It is *2, 4-dihydroxymercurianiline.* (Hg). It decomposes at 250° without melting. It is very little soluble in hot water and insoluble in alcohol.

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[66] Vecchiotti, *Gazz. chim. ital.* 44 II (1914), 35. *Chem. Zentr.* 1914 II 1350.

[67] Cf. Pesci, *Chem. Ztg.* 23 (1899), 58.

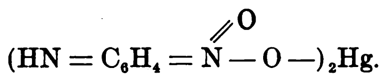
Theory of the Mechanism of the Mercuration of Aromatic Amines.[68]

It has been suggested that the mercuration of aromatic amines is always preceded by the *addition* of the inorganic mercury compound to the amino nitrogen forming an ammonium salt in which the positive group —HgX is attached to nitrogen. This group then rearranges to the ortho or para position in the ring in the same way that the chlorine of N-chloroacetanilide rearranges to give p-chloroacetanilide. That such preliminary addition is necessary for mercuration is practically proved by the fact that substituted anilines, such as p-nitro-dimethylaniline and p-nitro-diethylaniline, which are too weakly basic to form stable hydrochlorides, cannot be mercurated by treatment with mercuric acetate in aqueous alcohol. The corresponding monoalkyl anilines which do form hydrochlorides can be mercurated in the usual way. Moreover, the ortho and meta nitrodimethylanilines form hydrochlorides and can be mercurated. Another case which supports the theory is that of trimethylphenyl ammonium acetate. This substance obviously cannot add a molecule of mercuric salt. It gives no action with mercuric acetate and alcohol either on standing for months or on boiling for twenty-four hours.

Mercury Compounds from the Nitroanilines.[69]

The three nitroanilines react with mercuric acetate in methyl alcohol giving colored precipitates which are blackened at once by ammonium sulfide. Long standing in contact with the mother liquor changes these precipitates to substances which are stable to ammonium sulfide.

Recently more work has been done on the mercury derivatives of the nitroanilines.[70] The ortho and para compounds react with mercuric acetate in cold alcohol solution forming precipitates of a deep maroon color. This color is explained by formulating the substances as ortho and para quinone-imide-acinitro salts,



$$(\mathrm{HN} = \mathrm{C_6H_4} = \overset{\displaystyle /\!\!/^{\mathrm{O}}}{\mathrm{N}} - \mathrm{O} -)_2\mathrm{Hg}.$$

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[68] Kharasch and Jacobsohn, *J. Am. Chem. Soc.* 43 (1921), May ?

[69] Rother, *Dissert.* Berlin, 1911, p. 19.

[70] Private communication, Kharasch, Lommen, and Jacobsohn.

This seems more likely than the older formulation of the substances as N — Hg compounds.[71] Meta-nitroaniline under similar conditions gives a slightly yellow compound which probably consists of a mercuric acetate "salt" of the aniline, $NO_2 — C_6H_4 — NH_2.Hg(OAc)_2$.

If the reactions are carried out in boiling alcohol, mercuration of the nucleus takes place. Ortho nitroaniline reacts with one or two molecules of mercuric acetate giving *4-acetoxymercuri-2-nitroaniline* and *4, 6-diacetoxymercuri-2-nitroaniline.* Both these compounds are orange yellow in color. Treatment with sodium hydroxide changes them to bright scarlet compounds. These probably have a quinoid structure. Para nitroaniline gives two products, *2-acetoxymercuri-4-nitroaniline* and *2, 6-diacetoxymercuri-4-nitroaniline.* These compounds turn maroon red on treatment with sodium hydroxide. The former compound reacts with acetic anhydride giving *2-acetoxymercuri-4-nitroacetanilide,* a colorless substance. Treatment of the mercurated aniline with sodium thiosulfate gives *2, 2′-mercuribis-4-nitroaniline.* Meta nitroaniline gives two compounds, *4-acetoxymercuri-3-nitroaniline* and *4, 6-diacetoxymercuri-3-nitroaniline.* The former compound is yellow and the latter is reddish purple.

Mercury Derivatives of Monomethylaniline.[72]

p-Methylaminophenylmercuric acetate, $CH_3NH — C_6H_4 — HgOAc$.

An aqueous alcoholic solution of mercuric acetate is treated with an alcoholic solution of monomethylaniline. The product consists of colorless transparent leaflets which are insoluble in water and ether, easily soluble in hot alcohol and dilute acetic acid. M.P. 149° decomp.

Treatment with acetic acid and sodium nitrite gives a *mercurated nitrosamine,* $AcOHg — C_6H_4 — N(NO)CH_3$.[73] M.P. 183-4° decomp. (corr.) (NHg). The formation of this nitrosamine proves that the original mercury compound is a secondary amine and disproves Pesci's bimolecular formulas.[74]

p-Methylaminophenylmercuric hydroxide.

The acetate is treated with potassium hydroxide with the formation of an amorphous white powder insoluble in common solvents. When

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[71] Jackson and Peakes, *Am. Chem. J.* 39 (1907), 567.

[72] Pesci, *Gazz. chim. ital.* 23 II (1893), 521. *Chem. Zentr.* 1894 I 501. *Gazz. chim. ital.* 23 II (1893), 529. *Ber.* 27 R (1894), 128. Pesci, *Z. anorg. Chem.* 15 (1897), 216.

[73] Jacobs and Heidelberger, *J. Biol. Chem.* 20 (1915), 513.

[74] Cf. Dimroth, *Ber.* 35 (1902), 2039 ff.

heated with sodium sulfide it gives p-mercuribis-monomethylaniline, $Hg(C_6H_4-NHCH_3)_2$. Treatment with methyl iodide and then with potassium hydroxide and barium sulfhydrate gives the compound, $Hg[C_6H_4-N(CH_3)_3I]_2$, which is the same as that obtained from the para mercury compounds of aniline and dimethylaniline.

p-Methylaminophenylmercuric chloride.

The acetate is treated with sodium chloride solution. M.P. 108° decomp. It is an amorphous slightly yellow powder which is insoluble in water and alcohol. It turns green in light. The *bromide* is made in the same way and has similar properties. M.P. 120° decomp. The *nitrate* is made from the acetate and a large amount of cold dilute nitric acid. It forms colorless hexagonal leaflets which dissolve in hot water with decomposition. On heating it decomposes suddenly at 150°. The *sulfate* is prepared from the acetate by means of dilute sulfuric acid. It forms microscopic prisms which are soluble in dilute sulfuric acid. M.P. 130° decomp.

p-Mercuribis-monomethylaniline.

The hydroxide is treated with the calculated amount of sodium sulfide, heated, filtered, washed, dried, and extracted with hot benzene. The product forms colorless needles which are little soluble in alcohol, soluble in benzene, insoluble in ether. (CHHg). M.P. 179°.

Monomethylaniline and aqueous mercuric chloride give a yellowish precipitate which forms yellow needles from alcohol. No formula is given.[75]

p-Nitro-o-acetoxymercuri-monomethylaniline.[76]

p-Nitro monomethylaniline in alcohol is boiled with an aqueous solution of nine-tenths of a mole of mercuric acetate. The product is extracted with ether to remove unchanged material. The residue is crystallized from alcohol. A small amount of a dark red solid remains insoluble. It has not been studied. The product forms small yellow crystals. It is soluble in acetone and in hot alcohol containing a few drops of glacial acetic acid. (NHg). M.P. 197° decomp. Treatment with concentrated potassium hydroxide gives a brick red compound. Dilution restores the yellow color. The corresponding *chloride* is obtained from the mother liquors of the acetate by the addition

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[75] Lachowicz, *Monatsh.* 10 (1889), 893.

[76] Kharasch and Jacobsohn, *J. Am. Chem. Soc.* 43 (1921) May?

of sodium chloride solution. The product forms pale yellow crystals which are soluble in acetone and in boiling alcohol. (Cl). M.P. 215° decomp. Treatment with one molecule of bromine gives no definite product. Two molecules form 4-nitro-2, 6-dibromomonomethylaniline melting 112-13°.

Mercury Derivatives of Dimethylaniline.

p-Mercuribis-dimethylaniline.

Preparation.

1. From p-bromodimethylaniline and sodium amalgam.[77]
2. From p-dimethylaminophenylmercuric hydroxide and sodium sulfide.[78]

The finely powdered hydroxide is suspended in water and treated with the calculated amount of sodium sulfide. After several hours' heating the gray precipitate is filtered off, dried, and extracted with hot benzene leaving black flakes of mercuric sulfide. The benzene solution on cooling gives colorless needles.

It is an interesting fact that the R_2Hg compound is not obtained by heating p-dimethylaminophenylmercuric iodide with an excess of alcoholic potassium iodide. Considerable dimethylaniline is obtained.[79] This result is quite different from that obtained with a compound having the mercury ortho to the dimethylamino group. o-Iodomercuri-p-bromo-dimethylaniline reacts with potassium iodide giving the corresponding mercuribis compound in good yield.[80]

Properties.

p-Mercuribis-dimethylaniline separates from benzene in shining needle crystals containing one molecule of benzene which is lost on standing in air. It is little soluble in alcohol and ether, readily soluble in chloroform. (CHHg). M.P. 169°. It is slightly soluble in cold dilute hydrochloric acid and is reprecipitated by bases.

Reactions.

1. With acids.[81]

Hydrochloric acid in benzene reacts in the cold giving dimethyl-

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[77] Michaelis and Schenck, *Ber.* 21 (1888), 1501. *Ann.* 260 (1890), 6.

[78] Pesci, *Gazz. chim. ital.* 23 II (1893), 526. *Chem. Zentr.* 1894 I 501.

[79] Unpublished results, Whitmore and L. F. Howe.

[80] Whitmore, *J. Am. Chem. Soc.* 41 (1919), 1850.

[81] Michaelis and Schenck, loc. cit. Michaelis and Rabinerson, *Ber.* 23 (1890), 2342.

aniline and p-dimethylaminophenylmercuric chloride. Acetic acid gives mercuric acetate and dimethylaniline. The intermediate organomercuric acetate is not obtained.

2. With mercuric salts.[82]

Mercuric halides react readily in alcohol forming the corresponding p-dimethylaminophenylmercuric halides.

3. With phosphorus trichloride.[83]

The reaction takes place spontaneously with the evolution of heat even when diluted with benzene. The reaction is completed by heating in a sealed tube for three hours at 130°. The products are mercuric chloride and dimethylaminophosphenyl chloride,

$$(CH_3)_2N-C_6H_4-PCl_2.$$

4. With thionyl chloride.[84]

The two substances react on slight warming giving a bright yellow voluminous precipitate. This is probably

$$[(CH_3)_2N-C_6H_4-]_3S-O-Hg-C_6H_4-N(CH_3)_2.$$

When this precipitate is boiled with concentrated hydrochloric acid all the mercury appears in the ionic form. After treatment with hydrogen sulfide and filtration the filtrate gives the sulfine chloride,

$$[(CH_3)_2N-C_6H_4-]_3SCl.6H_2O.$$

5. With methyl iodide.[85]

The substances react in the cold forming the compound, $Hg[-C_6H_4-N(CH_3)_3I]_2$. It forms colorless crystals which turn yellow at 218° and melt at 230°. It is also obtained by treating the following substances with methyl iodide in methyl alcohol, then with alcoholic potassium hydroxide, and finally with barium sulfhydrate: the anhydride of p-aminophenylmercuric hydroxide, p-methylaminophenylmercuric hydroxide, and p-dimethylaminophenylmercuric hydroxide. When this quarternary iodide is treated with silver chloride and water it gives a solution of the corresponding chloride. This reacts with mercuric chloride giving a compound which melts with decomposition at 225°. This substance is given the formula of a double salt, $Hg[C_6H_4-N(CH_3)_3Cl]_2.HgCl_2$. It would seem likely that this

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[82] Michaelis and Schenck, *Ber.* 21 (1888), 1501. *Ann.* 260 (1890), 6. Michaelis and Rabinerson, *Ber.* 23 (1890), 2342.

[83] *Ibid.*

[84] Michaelis and Godchaux, *Ber.* 24 (1891), 758.

[85] Pesci, *Gazz. chim. ital.* 23 II (1893), 528.

formulation is not correct and that the product is the result of the usual reaction between R_2Hg and HgX_2, namely

$$ClHg—C_6H_4—N(CH_3)_3Cl.$$

p-Dimethylaminophenylmercuric acetate.[86]

Preparation.

1. Dimethylaniline is treated with mercuric acetate in 50 per cent alcohol. Small needle crystals soon separate. These are recrystallized from hot alcohol avoiding long heating which causes decomposition.

2. Dimethylaniline acetate is treated with mercuric oxide.[87]

Properties.

The acetate forms long colorless needles. (CHNHg). M.P. 165°. It is soluble in benzene, chloroform, hot alcohol, dilute acids, but insoluble in water. It does not react with cold ammonium sulfide.

Reactions.

1. Cold or hot potassium iodide in alcohol gives only the corresponding iodide and a very small amount of inorganic mercury.[88]

2. Potassium hydroxide gives p-dimethylaminophenylmercuric hydroxide.

p-Dimethylaminophenylmercuric hydroxide.

The acetate treated with hot aqueous potassium hydroxide gives a solution which on cooling deposits microscopic prisms. (CHNHg). M.P. 179° with decomposition after turning yellow about 150°. It is very little soluble in cold water but readily on heating. The solution is strongly alkaline. Treatment with 13 per cent sodium sulfide gives p-mercuribis-dimethylaniline.

p-Dimethylaminophenylmercuric chloride.

Preparation.

1. From the acetate in acetic acid treated with sodium chloride solution.

2. From p-mercuribis-dimethylaniline and mercuric chloride in alcohol.

[86] Pesci, *Z. anorg. Chem.* 15 (1897), 217. Dimroth, *Ber.* 35 (1902), 2044.

[87] Pesci, *Gazz. chim. ital.* 23 II (1893), 528.

[88] Dimroth, *Z. anorg. Chem.* 33 (1903), 314.

3. From p-mercuribis-dimethylaniline and a benzene solution of hydrogen chloride.

Properties and reactions.

The chloride gives white pearly leaflets from chloroform in which it is difficultly soluble. (NClHg). M.P. 225°. It is almost insoluble in alcohol, slightly soluble in benzene and chloroform. It dissolves in cold dilute hydrochloric acid and is reprecipitated by sodium carbonate.

The corresponding *bromide* is prepared from p-mercuribis-dimethylaniline and mercuric bromide in alcohol. It resembles the chloride. (NBr). M.P. 226°. The *iodide* is prepared like the bromide or by treating the acetate with potassium iodide. It resembles the chloride. (I). M.P. 195°.

Quarternary ammonium compounds related to p-mercuribis-dimethylaniline.

The *iodide*, $Hg[C_6H_4—N(CH_3)_3I]_2$.[89]

Preparation.

1. From p-mercuribis-dimethylaniline and methyl iodide.

2. From p-dimethylaminophylmercuric hydroxide and methyl iodide, followed by treatment with barium sulfhydrate.

3. From p-aminophenyl mercuric hydroxide or its anhydride and methyl iodide, potassium hydroxide, and barium sulfhydrate.

4. From p-methylaminophenylmercuric hydroxide and the same reagents.

In each of the last three preparations the first product is $IHg—C_6H_4—N(CH_3)_3I$. This reacts with the sulfhydrate giving mercuric sulfide and the corresponding R_2Hg compound.

Properties.

The quarternary iodide forms fine colorless flexible needles which are very little soluble in cold water, easily soluble in hot water and alcohol, but insoluble in chloroform and benzene. It is not changed by boiling potassium hydroxide. When heated slowly it turns brown at 218° and melts at 230°. Rapid heating gives a lower melting point.

The *chloride*, $Hg[C_6H_4—N(CH_3)_3Cl]_2$, is obtained in water solu-

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[89] Pescl, *Z. anorg. Chem.* 15 (1897), 218.

tion by treating the iodide with silver chloride. It reacts with bromine giving mercuric salts and p-bromophenyl trimethyl ammonium chloride. With mercuric chloride it gives the "double salt" melting at 225° with decomposition. The corresponding *hydroxide* is obtained from the iodide and silver oxide. The aqueous solution is strongly basic and caustic. It absorbs carbon dioxide rapidly.

p-Iodomercuriphenyl trimethyl ammonium iodide,

$$IHg—C_6H_4—N(CH_3)_3I.$$

p-Dimethylaminophenylmercuric hydroxide is treated with methyl iodide in cold methyl alcohol. The iodide forms hard greenish yellow branched prisms. It is insoluble in water, very soluble in acetone even cold, difficultly soluble in alcohol. It is best crystallized from alcohol. (CHIHg). M.P. 140° Treatment with barium sulfhydrate gives the corresponding R_2Hg compound, $Hg[C_6H_4—N(CH_3)_3I]_2$.

Mercury Derivatives of p-Bromodimethylaniline.[90]

p-Bromodimethylaniline reacts readily with a cold alcoholic solution of mercuric acetate containing a little acetic acid to prevent the alcoholysis of the mercuric salt. One hydrogen of the nucleus is replaced by the acetoxymercuri group.

o-Acetoxymercuri-p-bromo-dimethylaniline.

The product from the action of mercuric acetate on p-bromodimethylaniline forms white needle crystals. It is almost insoluble in water and petroleum ether. It is difficultly soluble in toluene, ethyl ether, and chloroform even on heating. It is fairly soluble on heating in ethyl acetate, benzene, and carbon tetrachloride. It is very soluble on heating in methyl alcohol, ethyl alcohol, and acetone. Carbon disulfide dissolves it readily even in the cold. It is best crystallized from methyl alcohol, ethyl alcohol, or benzene. The latter is the best solvent for its purification as it does not dissolve the mercurous acetate which is present as an impurity. It is also soluble in cold concentrated ammonium hydroxide. M.P. 144° (HgBr). The acetate reacts very slowly with sulfides. Its solution in ammonium hydroxide gives a white precipitate of the organomercuric sulfide when treated with hydrogen sulfide. This precipitate remains white for several

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[90] Whitmore, *J. Am. Chem. Soc.* 41 (1919), 1841.

hours. After standing for five hours at room temperature it turns gray. The acetate can be changed to other salts by the usual metathetical reactions. The *chloride* separates from alcohol or benzene in felted needles. M.P. 183° (BrClHg). The *bromide* crystallizes in larger needles than the chloride. It is more soluble in organic solvents. M.P. 182° (Hg). The *iodide* is even more soluble than the bromide. M.P. 169° (Hg). The *thiocyanate* resembles the halides. M.P. 135° (BrHg). The *hydroxide* is formed from the acetate and the calculated amount of sodium hydroxide in alcohol. It forms hard wart-like masses of crystals which are insoluble in all inert solvents. M.P. 162° (Hg). It dissolves in acetic acid and in ethyl acetate giving back the original acetate. The reaction of the hydroxide with an ester gives a new method for making organomercuric salts of organic acids. The *formate* is made by dissolving the hydroxide in an excess of ethyl formate. On cooling, fine felted needles separate. M.P. 145° (BrHg). The crystals turn black on standing. The formate is more soluble than the acetate. It is fairly soluble in water. Heating the formate in benzene and alcohol gives metallic mercury, p-bromodimethylaniline, and a mere trace of the corresponding mercuribis compound.

Mercuribis-p-bromo-dimethylaniline or 2, 2′-mercuribis-4-bromo-dimethylaniline.

It is prepared from the acetate by refluxing with potassium iodide in alcohol for 8 hours. Yield 86 per cent. It forms white needle crystals. M.P. 123° (BrHg). It is more soluble than the acetate, being soluble even in the cold in benzene, toluene, ether, carbon disulfide, and acetone.

Treatment of the organomercuric acetate with sodium thiosulfate and with sodium sulfide gives smaller yields of the mercury diphenyl derivative.

The mercury diphenyl compound reacts quantitatively with mercuric chloride, bromide, iodide, and thiocyanate forming the corresponding R — Hg — X compounds.

Mercury Derivatives of Nitro Dimethylanilines.[91]

Of the three isomeric nitro dimethylanilines the para compound alone cannot be mercurated by means of mercuric acetate. This property of the para compound is connected with its extremely weak

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[91] Kharasch and Jacobsohn, *J. Am. Chem. Soc.* 43 (1921), May?

basic properties and consequent inability to form salts. It seems almost certain that the entrance of mercury into the nucleus of an aromatic amine is preceded by the formation of a "salt" by the addition of the inorganic mercury compound to the amino nitrogen. The positive —HgX group then rearranges to the nucleus in much the same way as does the chlorine in N— chloroacetanilide.

o-Nitro-p-acetoxymercuri-dimethylaniline.

o-Nitro dimethylaniline dissolved in a small volume of alcohol is boiled with nine-tenths of a mole of mercuric acetate. In half an hour a side test with ammonium sulfide gives no black precipitate. A small amount of mercurous acetate is removed by filtering the hot solution. Crystals separate on cooling. The product is yellow and is soluble in the common organic solvents. (NHg). M.P. 160°. The corresponding *chloride* is obtained by treating the filtrate from the original reaction mixture with sodium chloride solution. The product is red and amorphous. (NCl). M.P. 185° decomp.

m-Nitro-p-acetoxymercuri-dimethylaniline.

m-Nitro dimethylaniline is treated with mercuric acetate in the usual way. The reaction is complete after half an hour's boiling. The product forms brilliant orange needles which are soluble in the common organic solvents. (NHg). M.P. 140°. The *chloride* is obtained from the mother liquor in the usual way. It is red and amorphous (Cl). M.P. 220° decomp.

Mercury Derivatives of Monoethylaniline.[92]

p-Mercuribis-monoethylaniline.

The finely powdered hydroxide, $C_2H_5NH—C_6H_4—HgOH$, is heated with the calculated amount of sodium sulfide solution. The dark precipitate is dried and extracted with boiling xylene. The extracts on cooling give colorless crystals of the mercury diphenyl derivative. These are fairly soluble in benzene and slightly soluble in alcohol. (CHHg). M.P. 166°.

p-Ethylaminophenylmercuric acetate.

An alcohol solution of monoethylaniline is treated with a solution of mercuric acetate in dilute alcohol. Colorless transparent prisms separate which are insoluble in cold water, easily soluble in benzene, prac-

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[92] Pesci, loc. cit.

tically insoluble in ether. (CHHg). M.P. 130°. The acetate is apparently decomposed by hot water.

p-Ethylaminophenylmercuric hydroxide.

The acetate is treated with potassium hydroxide on the water bath. The clear solution deposits colorless heavy needles on cooling. It is little soluble in cold water, soluble hot, but insoluble in ether. The water solution has a strong alkaline reaction. (CHHg). It decomposes at 145° without melting.

Treatment with sodium sulfide changes the hydroxide to p-mercuribis-monoethylaniline. An excess of methyl iodide gives a yellow powder which is probably $IHg - C_6H_4 - N(CH_3)_2(C_2H_5)I$. When this is treated with barium sulfhydrate it gives the corresponding R_2Hg compound, $Hg[C_6H_4 - N(CH_3)_2(C_2H_5)I]_2$.

p-Ethylaminophenylmercuric chloride.

The acetate is treated with calcium chloride in alcohol. The chloride is recrystallized from alcohol from which it forms colorless hexagonal tablets. (Hg). M.P. 143°. It is insoluble in cold water and decomposed by hot water.

Quarternary ammonium compounds related to p-mercuribis-monoethylaniline.

The *iodide*, $Hg[C_6H_4 - N(CH_3)_2(C_2H_5)I]_2$ is prepared as just described. It forms long colorless silky needles. (CHIHg). M.P. 202°. It can be crystallized from hot water. Hot bases have no effect on it. The corresponding *chloride* is made by treating the iodide with silver chloride. It forms long colorless needles which are readily soluble in water. The chloride gives a *"double salt"* with mercuric chloride which melts at 169° and is slightly soluble in alcohol but is insoluble in cold water. This substance may very likely be a true organomercuric salt, $ClHg - C_6H_4 - N(CH_3)_2(C_2H_5)Cl$. The *hydroxide*, $Hg[C_6H_4 - N(CH_3)_2(C_2H_5)OH]_2$, is made from a water solution of the iodide and silver oxide. The resulting solution is strongly basic and caustic. It absorbs carbon dioxide readily.

Mercury Derivatives of p-Nitro Monoethylaniline.[93]

p-Nitro-o-acetoxymercuri-monoethylaniline.

p-Nitro monoethylaniline is treated with mercuric acetate in aqueous alcohol in the usual way. The product crystallizes from alcohol

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[93] Kharasch and Jacobsohn, *J. Am. Chem. Soc.* 43 (1921), May?

in small yellow crystals. It is soluble in acetone. (NHg). M.P. 183°. Treatment with concentrated potassium hydroxide gives a brick red compound which turns yellow on dilution.

The easy mercuration of the p-nitro *mono*ethylaniline is in sharp contrast to the fact that the corresponding p-nitro *di*ethylaniline cannot be mercurated. This difference is due to the difference in the basic properties of the two substances. p-Nitro diethylaniline, like p-nitro dimethylaniline, does not form salts readily. The monoalkylated compounds do form salts and can be mercurated.

The corresponding *chloride* is prepared from the mother liquor in the usual way. It is an amorphous yellow solid. (Cl). It is soluble in acetone and in hot alcohol. M.P. 218° decomp. Treatment with bromine gives 4-nitro-2, 6-dibromomonoethylaniline identical with the product obtained by the direct bromination of p-nitro monoethylaniline.

Mercury Derivatives of Diethylaniline.

p-Mercuribis-diethylaniline.[94]

Preparation.

1. From diethylaminophenylmercuric hydroxide and the calculated amount of sodium sulfide heated for several hours on the water bath. The precipitate is dried and extracted with hot benzene.
2. From p-diethylaminophenylmercuric chloride and an excess of concentrated sodium thiosulfate solution.[95]
3. From p-bromodiethylaniline and sodium amalgam.

Properties.

It forms colorless efflorescent prisms which are soluble in ether, insoluble in alcohol, fairly soluble in benzene. (CHHg). M.P. 160.6°. When treated with methyl iodide it gives the corresponding quarternary ammonium compound.

p-Diethylaminophenylmercuric acetate.

Diethylaniline is treated with mercuric acetate in the usual way. The product crystallizes from alcohol in long colorless needles which are insoluble in water, soluble in ether, alcohol, and dilute acetic acid, very soluble in benzene. M.P. 104.4° (not 164°). It decomposes with evolution of gas at 182°.

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[94] Pesci, loc. cit.

[95] Pigorini, *Gazz. chim. ital.* 24 II (1894), 465. *Ber.* 28 R (1895), 114.

p-Diethylaminophenylmercuric hydroxide.

The acetate is treated with potassium hydroxide in the usual way. The product turns brown at 125° but does not melt (165°?). It reacts with sodium sulfide forming p-mercuribis-diethylaniline. With methyl iodide and methyl alcohol it forms a yellow powder from which barium sulfhydrate forms the compound, $Hg[C_6H_4-N(CH_3)(C_2H_5)_2I]_2$.

p-Diethylaminophenylmercuric chloride.

An acetic acid solution of the acetate is treated with potassium chloride. The product forms sharp colorless needles which are little soluble in cold water, fairly soluble hot, soluble in hot dilute alcohol. M.P. 164.5° (Hg). The chloride reacts with a warm sodium carbonate solution forming a complex *oxide*, $[(CH_3)_2N-C_6H_4-Hg-]_2O$.[96]

Quarternary ammonium compounds related to p-mercuribis-diethylaniline.

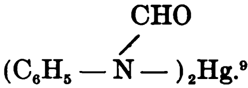
The *iodide*, $Hg[C_6H_4-N(CH_3)(C_2H_5)_2I]_2$, is prepared by treating p-diethylaminophenylmercuric hydroxide with methyl iodide and then with barium sulfhydrate. It forms small colorless prisms which are easily soluble in hot water, little in cold, little in alcohol, insoluble in ether and benzene. M.P. 203° decomp. (CHIHg). 50 per cent sodium sulfide removes the mercury entirely forming phenyl methyl diethyl ammonium iodide.

The corresponding *chloride* is prepared from the iodide by silver chloride. It forms good crystals which are very deliquescent. It reacts with mercuric chloride giving a *"double salt"* which softens at 168° and decomposes about 200°. This substance may be a compound, $ClHg-C_6H_4-N(CH_3)(C_2H_5)_2Cl$. The corresponding *hydroxide* is made from the iodide by silver oxide. It gives a strongly alkaline solution.

Mercury Derivatives of Acid Anilides.

N — Hg Compounds.

N-Mercuribis-formanilide,



$(C_6H_5-\overset{CHO}{N}-)_2Hg$.[97]

Alcoholic solutions of formanilide and mercuric bromide are mixed and treated with the calculated amount of sodium ethylate. The clear

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[96] Pigorini, loc. cit.

[97] Wheeler and McFarland, *Am. Chem. J.* 18 (1896), 542.

solution is precipitated by water. Colorless needles are obtained which melt at 194° (NHg). When the product is suspended in benzene and treated with benzoyl chloride a precipitate is formed. This is *N-chloromercuriformanilide,* $C_6H_5 — N(HgCl) — CO — H$. This compound can also be prepared from formanilide treated with one molecule of mercuric chloride and one molecule of sodium ethylate. The corresponding *bromide* and *iodide* are obtained by adding the proper halogen in carbon disulfide to N-mercuribisformanilide.

If formanilide in alcohol is treated with mercuric acetate and evaporated colorless slender prisms separate. These can be recrystallized from alcohol. (Hg). The product is believed to be N-acetoxymercuriformanilide. It might, however, be a C — Hg compound.

N-Mercuribis-acetanilide.[98]

Acetanilide is fused with yellow mercuric oxide. The product is crystallized from alcohol in small colorless needles. M.P. 215° decomp. It reacts at once with hydrogen sulfide. Acid chlorides give mixed anilides and probably the N — HgCl compound of acetanilide. It reacts with sodium thiosulfate, potassium iodide, and ammonium bromide as do all N — Hg compounds giving the corresponding inorganic base, a mercuric salt, and the N — H compound, in this case, acetanilide. This reaction may be illustrated by potassium iodide,

$$[C_6H_5 — N(COCH_3) —]_2Hg + 2KI + 2H_2O \rightarrow$$
$$2C_6H_5 — NH — COCH_3 + 2KOH + HgI_2.$$

N-Mercuribis-methacetin, $[CH_3O — C_6H_4 — N(COCH_3) —]_2Hg$.[99]

Methacetin is treated with mercuric chloride and sodium carbonate. The product forms sharp colorless tufted needles. (Hg). M.P. 191°. It reacts in the usual way with sodium thiosulfate, potassium iodide, and ammonium bromide giving the corresponding base and methacetin.

C — Hg Compounds of the Acid Anilides.

p-Mercuribis-acetanilide.[100]

The corresponding hydroxide, $CH_3CO — NHC_6H_4 — HgOH$, is treated with the calculated amount of sodium sulfide or barium sulf-

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[98] Oppenheim and Pfaff, *Ber.* 7 (1874), 624. Piccinini, *Gazz. chim. ital.* 24 II (1894), 453. *Chem. Zentr.* 1895 I 335. Wheeler and McFarland, *Am. Chem. J.* 18 (1896), 542. Wheeler, *Am. Chem. J.* 18 (1896), 696. Pesci, *Gazz. chim. ital.* 27 I (1897), 568.

[99] Prussia, *Gazz. chim. ital.* 28 II (1898), 123. *Chem. Zentr.* 1898 II 928.

[100] Pesci, *Gazz. chim. ital.* 24 II (1894), 449. *Z. anorg. Chem.* 15 (1897), 223. *Gazz. chim. ital.* 29 I (1899), 394. *Z. anorg. Chem.* 32 (1902), 232.

hydrate. It can also be prepared by fusing acetanilide with mercuric acetate and then treating the p-acetoxymercuriacetanilide so obtained with sodium hydroxide and sodium thiosulfate. It forms long needle crystals which are little soluble in alcohol even hot, insoluble in ether, benzene, and chloroform. M.P. 244-6°. Alcoholic potassium hydroxide in a tube at 100° gives p-mercuribis-aniline.

p-Acetaminophenylmercuric acetate.[101]

A boiling aqueous solution of acetanilide is treated with one molecule of mercuric acetate in small portions. The boiling is continued until a side test with a base gives no mercuric oxide. On cooling, shiny colorless plates separate. These are soluble in hot water, insoluble in benzene. M.P. 218-20°. The corresponding *chloride*, $CH_3CO — NHC_6H_4 — HgCl.H_2O$, is prepared from the acetate and calcium chloride in alcohol solution. It forms colorless microscopic needles. These are insoluble in water, more soluble in alcohol. It loses its crystal water at 110°. M.P. 250°.

Acetanilide fused with an excess of mercuric acetate gives various highly mercurated products. A dimercurated and a pentamercurated product have been isolated.[102]

Mercury Derivatives of Diphenylamine.

p-Mercuribis-diphenylamine, $Hg(C_6H_4 — NH — C_6H_5)_2$.[103]

p-Hydroxymercuridiphenylamine, $C_6H_5 — NH — C_6H_4 — HgOH$, is heated with concentrated sodium thiosulfate forming a white powder. This is very little soluble in methyl and ethyl alcohols, even on boiling. It is soluble in hot benzene and easily soluble in chloroform. Ligroin added to the solution in chloroform causes the separation of good crystals. (Hg). M.P. 182.5°.

p-Hydroxymercuri-diphenylamine.

The acetate obtained from diphenylamine and mercuric acetate is ground into a paste with concentrated potassium hydroxide and allowed to stand for 24 hours. A white granular amorphous substance is formed which is insoluble in all common solvents. It dissolves enough

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[101] Pesci, *Z. anorg. Chem.* 15 (1897), 222. Dimroth, *Ber.* 35 (1902), 2037.

[102] Hoff and Rossi, *Chem. Zentr.* 1912 II 2070. Pesci, *Chem. Ztg.* 23 (1899), 58. *Chem Zentr.* 1899 I 527.

[103] Prussia, *Gazz. chim. ital.* 28 II (1898), 129. *Chem. Zentr.* 1898 II 928.

in water to give an alkaline reaction. (Hg). It decomposes below 200° without melting.

p-Acetoxymercuri-diphenylamine.

An alcoholic solution of diphenylamine is added to a solution of mercuric acetate in 50 per cent alcohol containing a little acetic acid. Heat is evolved and the solution turns yellow. Soon small plates of the acetate separate. These are recrystallized from hot alcohol. They are insoluble in water, slightly soluble in methyl and ethyl alcohols, and in hot benzene. (CHHg). M.P. 178°. The corresponding *chloride* is made from the acetate and calcium chloride in alcohol. It is very slightly soluble in methyl and ethyl alcohols, hot chloroform, less soluble in benzene and ether, insoluble in water. (ClHg). It softens at 232° and decomposes at 240° without melting.

2, 2′, 4, 4′-Tetrachloromercuri-diphenylamine,

$(ClHg)_2C_6H_3 — NH — C_6H_3(HgCl)_2$.[104]

Diphenylamine is heated with mercuric chloride and the mixture is poured into acetic acid and boiled for some time. The residue is washed thoroughly with glacial acetic acid to remove all unchanged diphenylamine. The product is a yellow amorphous powder which does not melt at 260° and is insoluble in common solvents. (NClHg).

Boiling pyridine gives mercuric chloride and a product which is possibly a *mercazine,* containing mercury and nitrogen in a six membered ring. Treatment with sodium thiosulfate gives a complicated compound containing mercury with both valences attached to carbon. Its structure has not been settled.

Treatment of the tetrachloride with a mixture of sulfuric and nitric acids gives a compound containing 3 — HgCl groups and 2 nitro groups for each diphenylamine residue. The position of the nitro groups is not settled. Treatment of this nitro compound with sodium thiosulfate gives a complicated substance which is designated as "Mercuri-bis-3-dinitro(?)mercazine." Its structure is not definitely known. It is insoluble in all common solvents.

p-Mercuribis-methyldiphenylamine, $Hg[C_6H_4 — N(CH_3) — C_6H_5]_2$.

The corresponding hydroxide, $C_6H_5 — N(CH_3) — C_6H_4 — HgOH$, is treated with a 25 per cent sodium thiosulfate solution. The clear solution soon becomes turbid and deposits a white powder. This is

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[104] Kharasch and Piccard, *J. Am. Chem. Soc.* 42 (1920), 1861.

dried and dissolved in hot benzene in which it is readily soluble. The solution is cooled and treated with two volumes of ligroin. Colorless plates separate. (Hg). M.P. 138-9°.

p-Acetoxymercuri-methyldiphenylamine,

$$C_6H_5 - N(CH_3) - C_6H_4 - HgOAc.$$

Methyldiphenylamine is treated with mercuric acetate in the usual way. The product forms slightly yellow crystals from hot alcohol. M.P. 128° (Hg). It is insoluble in water and benzene, slightly soluble in methyl and ethyl alcohols. The corresponding *hydroxide* is made from the acetate and concentrated potassium hydroxide. It forms a white amorphous powder insoluble in all solvents.

Mercury Derivatives of Anilido Fatty Acids and their Esters.

2-Acetoxymercuriphenyl glycine ethyl ester,

$$AcOHg - C_6H_4 - NH - CH_2CO_2C_2H_5.$$[105]

Preparation.

The ethyl ester of phenyl glycine dissolved in methyl alcohol is stirred with one molecule of mercuric acetate in methyl alcohol containing a little acetic acid. The cloudy yellow oil which forms dissolves on stirring. In 10 to 15 minutes no mercuric ions are left as shown by a side test with sodium hydroxide. On cooling the mixture, pale yellow crystals separate. Yield 82 per cent. The mother liquors give a small amount of another product which has not been identified. The acetate is recrystallized from chloroform.

Properties.

The acetate forms pale yellow crystals. After recrystallization from chloroform, all of the solvent must be removed. It softens at 128° and melts at 131° if free from chloroform. It is easily soluble in organic solvents especially in hot chloroform. It dissolves in hot water and on cooling separates as an oil.

Reactions.

1. With halogens.

Bromine and iodine give halogenated phenyl glycine esters which melt at 83° and 87° respectively. As they are probably the ortho compounds the ortho structure is assigned to the mercury compound.

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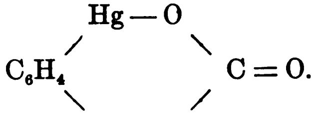
[105] Schoeller and Schrauth and Goldacker, *Ber.* 44 (1911), 1301. Schoeller and Schrauth, D. R. P. 248,291. *Chem. Zentr.* 1912 II 211.

2. With halide salts.

Alcoholic solutions of the alkali halides give the corresponding — HgX compounds.

3. Saponification.

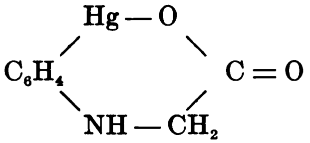
Treatment with sodium hydroxide and then with acid gives the anhydride of *2-hydroxymercuriphenyl glycine,*



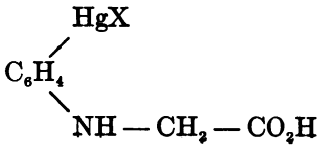
2-Chloromercuriphenyl glycine ethyl ester.

An alcoholic solution of the acetate is treated with the calculated amount of sodium chloride dissolved in water. More water is added. Fine needles separate. The chloride is soluble in organic solvents especially ethyl acetate. It is best crystallized from methyl alcohol. It sinters at 149° and melts at 151°. Heated above its melting point it gradually solidifies and then decomposes above 200° (NClHg). It forms rhombic tablets from ethyl acetate. The corresponding *bromide* is prepared like the chloride and has similar properties. It sinters 144° and melts 146° (BrHg). The *iodide* resembles the chloride and bromide. (Hg). It sinters 136-7° and melts about 139°.

Anhydride of 2-hydroxymercuriphenyl glycine,



The finely powdered acetate is suspended in water and heated with one molecule of sodium hydroxide. The solid turns bright yellow but does not dissolve. This substance is probably the — HgOH compound of the ester. Another molecule of sodium hydroxide is added and the mixture is boiled one or two minutes. All dissolves. The solution now contains the sodium salt of 2-hydroxymercuriphenyl glycine. This solution is treated with 1.25 equivalents of normal sulfuric acid. A white amorphous precipitate forms. It is soluble in excess of acid probably due to the formation of salts of the type,



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Yield 91 per cent. The anhydride decomposes at 223° (corr. 228°) (CHNHg). It is soluble in one molecule of sodium hydroxide. This solution gives precipitates with solutions of some metal salts. Precipitates are obtained with solutions of salts of lead, copper, iron, calcium, silver, and platinum. The copper salt has been purified and analyzed. It decomposes about 190-194°.

(?)Chloromercuriphenyl glycine.[106]

When the compound, $Cl_2As — C_6H_4 — NH — CH_2CO_2H$, is heated with mercuric chloride a white precipitate containing mercury is formed. It is soluble in alkali and probably has mercury attached to the nucleus.

Another mercury compound is obtained by heating p-arsenophenyl glycine,

$HO_2C.CH_2 — NH — C_6H_4 — As = As — C_6H_4 — NH — CH_2CO_2H$, with alkali and mercuric oxide. The product is precipitated by the addition of acid. It may be the R_2Hg compound corresponding to phenyl glycine.

α-Anilidopropionic ethyl ester reacts with one molecule of mercuric acetate in methyl alcohol forming a monomercurated product which cannot be separated from some di-product formed at the same time. The reaction is complete in 20 minutes. The crude acetate is very soluble in organic solvents.

(2-Chloromercuriphenyl-α-amino) propionic ethyl ester,

$ClHg — C_6H_4 — NH.CH(CH_3) — CO_2C_2H_5$.[107]

An alcoholic solution of the impure acetate obtained from equal molecules of mercuric acetate and the anilido ester is treated with the calculated amount of sodium chloride. The precipitate is recrystallized from 80 per cent alcohol. (CHNClHg). It is only slightly soluble in organic solvents. M.P. 164°. The mercury is assumed to be in the ortho position by analogy to the corresponding phenyl glycine compound.

(2, 4-Diacetoxymercuriphenyl-α-amino) propionic ethyl ester.

The anilido ester is treated with two molecules of mercuric acetate in methyl alcohol. The reaction is complete in about one hour. The yield of crude product is about 80 per cent. This consists of about

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[106] D. R. P. 272,289. *Chem. Zentr.* 1914 I 1469.

[107] Schoeller, Schrauth, and Goldacker, loc. cit. 1305.

equal amounts of a crystalline soluble form and an amorphous insoluble form of the diacetate. The former is removed by repeated extractions with hot methyl alcohol containing a little acetic acid. This solution is cooled to obtain crystals. (CHNHg). M.P. 184°. The insoluble substance has the same melting point and the same percentage of mercury as the crystalline form. It may be a polymer. The two diacetates give the same products when boiled with sodium chloride or bromide.

(2, 4-Dichloromercuriphenyl-α-amino) propionic ethyl ester.

The diacetate is treated with the calculated amount of sodium chloride solution. The precipitate is purified by dissolving in ethyl acetate and precipitating by the addition of low boiling ligroin. It forms small needles. The same product is obtained from the amorphous insoluble form of the diacetate by boiling with dilute sodium chloride for 15 or 20 minutes. (Hg). M.P. 128-130°. The corresponding *dibromide* is prepared from the crystalline or the amorphous diacetate. (Hg). It melts about 128°.

Anhydride of (2, 4-dihydroxymercuriphenyl-α-amino) propionic acid.

The diacetate obtained from α-anilidopropionic ethyl ester and two molecules of mercuric acetate is suspended in water and boiled with 3.25 molecules of sodium hydroxide to form a clear solution and then acidified with 1.25 equivalents of normal sulfuric acid. The white amorphous solid decomposes at 218° (corr. 223°) (CHNHg). The anhydride absorbs water readily. As this is not usually true of the anhydrides or inner salts of hydroxymercuri acids the loss of water in this case may take place between the two — HgOH groups instead of between the — HgOH group and the carboxyl group.

α-Anilidobutyric ethyl ester treated with one molecule of mercuric acetate gives a dimercurated compound and unchanged ester. No monomercurated product is obtainable in methyl alcohol solution.

(2, 4-Diacetoxymercuriphenyl-α-amino) butyric ethyl ester,

$$(AcOHg)_2C_6H_3 - NH.CH(C_2H_5) - CO_2C_2H_5.$$

The reaction of the anilido ester with two molecules of mercuric acetate in dilute methyl alcohol is complete in about half an hour. Cooling gives a crystalline product. Yield 82 per cent. It is easily soluble in methyl and ethyl alcohols, and in chloroform, but only slightly soluble in other solvents. It is best recrystallized from methyl alcohol. (CHNHg). It sinters at 150° and melts at 153°.

(2, 4-Dichloromercuriphenyl-α-amino) butyric ethyl ester.

The diacetate is treated with sodium chloride. The dichloride is easily soluble in common solvents especially on heating. It is best purified by dissolving in ethyl acetate and adding low boiling ligroin. (Hg). On rapid heating it softens at 124° and melts at 126°. The corresponding *dibromide* and *diiodide* are made in the same way and have similar properties. Bromide M.P. 126°, Iodide M.P. 119°.

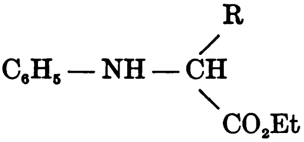
(2, 4-Dihydroxymercuriphenyl-α-amino) butyric acid and its *anhydride.*

The anhydride is prepared from the ester in the usual way. Yield 90 per cent. The anhydride turns yellow at 200° and decomposes at 205° (corr. 209°) (CHNHg). If allowed to stand in the air the anhydride absorbs one molecule of water in two hours but gives no further absorption on longer standing. As in the case of the propionic compound this easy hydration and dehydration may indicate that the water is lost between the two hydroxymercuri groups.

α-Anilido-isovalerionic ethyl ester reacts with mercuric acetate giving a dimercurated product even when an excess of the ester is used. No mono compound can be obtained.

(2, 4-Diacetoxymercuriphenyl-α-amino) isovalerianic ethyl ester.

The reaction between the anilido ester and two molecules of mercuric acetate in dilute methyl alcohol is complete in about half an hour. Yield 86 per cent. The product is recrystallized from methyl alcohol. It is soluble in ethyl alcohol and in chloroform, especially on heating. (CHNHg). M.P. 125°. The corresponding *chloride* is made from the acetate in the usual way. M.P. 121°. The *bromide* occurs in two forms. When the crude substance is heated with ethyl acetate part of it is precipitated in an amorphous form. This decomposes at 215°. The ethyl acetate mother liquors treated with low boiling ligroin give crystals which melt at 134°. The *iodide* is like the bromide but is slightly yellow and occurs only in a crystalline form. M.P. 128°. The *anhydride* is prepared in the usual way. It resembles the corresponding butyric acid compound in absorbing water readily from the air. (CHNHg). It decomposes at 221° (corr. 226°).

The foregoing studies on the mercuration of alpha anilido esters in dilute methyl alcohol with one molecule of mercuric acetate have disclosed some interesting regularities. The esters used have the general formula  $C_6H_5—NH—CH(R)(CO_2Et)$. When $R = H$ a monomercurated product is obtained. If $R = CH_3$ a mixture of mono and diproducts is obtained. If $R = C_2H_5$ or $i—C_3H_7$ only disubstitution products can be obtained.

Mercury Derivatives of the Toluidines.

Derivatives of o-Toluidine.[108]

The reaction between o-toluidine and one molecule of mercuric acetate in dilute methyl alcohol gives a product containing 15 per cent of mono- and 85 per cent of dimercurated compounds.

3-Methyl-4-aminophenylmercuric acetate.

A solution of three molecules of ortho toluidine in alcohol is added rapidly to a solution of mercuric acetate in 50 per cent alcohol. The precipitate is recrystallized from 50 per cent alcohol and then from absolute alcohol to separate it from a small amount of the dimercurated product. It is easily soluble in hot water, soluble in alcohol, difficultly soluble in ethyl acetate. It decomposes in a vacuum at 100°. If put in a bath at 140° it melts at 145° (NHg).

The acetate can be diazotized in the usual way and coupled with phenol, yielding *2-methyl-4-acetoxymercuri-4′-hydroxyazobenzene*, $AcOHg(CH_3)C_6H_3—N=N—C_6H_4OH$. (NHg).

3-Methyl-4-aminophenylmercuric chloride.

The alcoholic mother liquor from the preparation of the dimercurated compound is treated with sodium chloride solution. The dried precipitate is extracted with hot ethyl acetate and then recrystallized from absolute alcohol. It forms shining needles. (CHClHg). M.P. 175°. When treated with acetic anhydride it gives a *diacetyl derivative* thus proving that the original mercury compound contained a free amino group.[109]

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[108] Schoeller, Schrauth, and Rother, *Ber.* 45 (1912), 2812. J. Rother, *Dissert.* Berlin 1911, p. 24. Jacobs and Heidelberger, *J. Biol. Chem.* 20 (1915), 519.

[109] Jacobs and Heidelberger, loc. cit.

Diacetoxymercuri-o-toluidine.

Methyl alcohol solutions of equal molecules of o-toluidine and mercuric acetate react completely in a few minutes. The chief product is the dimercurated compound. It is recrystallized from methyl alcohol. It decomposes 223°. It is insoluble in most solvents except hot methyl alcohol, it dissolves readily in acids, ammonium hydroxide, amines, etc. A better yield is obtained by using two molecules of mercuric acetate.

The diacetate can be changed to the corresponding *chloride, bromide, iodide,* and *hydroxide* by double decomposition reactions. The hydroxide gives an anhydride by loss of water between the NH_2 group and one of the — HgOH groups. When this *anhydride* is treated with an excess of acetic anhydride an *acetylated diacetate* is formed, $(AcOHg)_2C_6H_2(CH_3)-NHCOCH_3$. This gives the corresponding *chloride, bromide,* and *iodide.*[110]

Dihydroxymercuri-o-toluidine.

The diacetate is suspended in water and heated with sodium hydroxide to about 90° until almost entirely dissolved. After filtering the solution is cooled slowly giving colorless needles. If dried at 100° or in a vacuum, or even if treated with absolute alcohol it loses water and changes to an intense canary yellow. The molecule of water is probably lost between the amino group and the ortho hydroxymercuri group. (Anhydride, CHNHg.)

Double salts of o-toluidine and mercuric halides.[111]

Derivatives of m-Toluidine.[112]

No monomercurated product has been obtained from m-toluidine. The reaction between equivalent amounts of m-toluidine and mercuric acetate gives a dimercurated product. An excess of mercuric acetate gives a trisubstitution product.

Diacetoxymercuri-m-toluidine.

Equal molecules of m-toluidine and mercuric acetate are allowed to react in methyl alcohol. The product forms colorless crystals which

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[110] J. Rother, loc. cit.

[111] Klein, *Ber.* 13 (1880), 835. Lachowicz, *Monatsh.* 10 (1889), 892.

[112] Schoeller, Schrauth, and Rother, *Ber.* 45 (1912), 2812. Rother, *Dissert.* Berlin 1911, p. 31.

are insoluble in the common solvents except methyl and ethyl alcohols. It is also soluble in dilute alcohol and ammonium hydroxide. It is stable to ammonium sulfide. Double decomposition yields the corresponding *halides.* Sodium hydroxide yields an amorphous *hydroxide.* The diacetate melts at a high temperature with decomposition. (CHHg). No monomercury compound is obtained from the mother liquors.

Triacetoxymercuri-m-toluidine.

m-Toluidine is treated with a large excess of mercuric acetate in dilute methyl alcohol. The product is insoluble in common organic solvents. It is soluble in ammonium hydroxide and slightly soluble in water. Boiling with ammonium sulfide gives mercuric sulfide. (CHHg).

Derivatives of p-Toluidine.[113]

p-Toluidine reacts with mercuric acetate giving a monomercury product. Heating with a large excess of mercuric acetate gives a more highly mercurated product which has not been obtained pure.

Acetoxymercuri-p-toluidine.

A solution of mercuric acetate in 50 per cent alcohol is treated with an alcoholic solution of p-toluidine. Leaflets soon separate. After two days the product is filtered and purified by dissolving in ammonium acetate and ammonium hydroxide and precipitating by acetic acid. It forms white crystals insoluble in water, soluble in benzene, alcohol, ether, and ammonium hydroxide. (CHHg). M.P. 184°. It can also be prepared from p-toluidine acetate and mercuric oxide.

When an excess of mercuric acetate reacts with p-toluidine a white solid is obtained which reacts at once with cold ammonium sulfide. It may have mercury attached to nitrogen as well as to the nucleus. No satisfactory analyses have been obtained.

Hydroxymercuri-p-toluidine.

The acetate dissolves in concentrated potassium hydroxide giving a clear solution which slowly deposits yellowish laminæ. The hydroxide is insoluble in common solvents. Heat turns it brown at 120°.

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[113] Pesci, *Gazz. chim. ital.* 28 II (1898), 101. *Z. anorg. Chem.* 17 (1898), 276. Reitzenstein and Stamm, *J. prakt. Chem.* (2) 81 (1910), 159. Schoeller, Schrauth, and Rother, loc. cit. Rother, loc. cit. Vecchiotti, *Gazz.* 48 II (1918), 80. *Chem. Abst.* 13 (1918), 1450.

M.P. 212-3°. It dissolves enough in water to give a strong alkaline reaction. (CHHg). When treated with sodium thiosulfate it gives mercuribis-p-toluidine.

Chloromercuri-p-toluidine.

The acetate and calcium chloride are allowed to react in alcohol. The chloride forms prismatic needles. It is insoluble in water, fairly soluble in alcohol. (CHHg). M.P. 170°.

Mercuribis-p-toluidine.

The hydroxide is treated with concentrated sodium thiosulfate solution in the usual way. The product forms a white powder which is soluble in alcohol but insoluble in other solvents. (CHHg). M.P. 156°.

When dissolved in pyridine and treated with a methyl alcohol solution of dinitrophenyl pyridine chloride it gives a dark solution which deposits a brown powder which is soluble in acetone and chloroform. M.P. 133°.[114]

Double salts of p-toluidine and mercuric salts.[115]

Mercury Derivatives of Dimethyl-p-toluidine.[116]

Acetoxymercuri dimethyl-p-toluidine.

Dimethyl-p-toluidine is treated with mercuric acetate in the usual way. Fine colorless needles gradually separate. These are recrystallized from boiling benzene. It is insoluble in water, fairly soluble in ethyl alcohol, very soluble in methyl alcohol. (CHHg). M.P. 131.5°.

Hydroxymercuri dimethyl-p-toluidine.

The acetate is treated with concentrated potassium hydroxide. The hydroxide forms fine colorless needles. It is hardly soluble in cold water but is a little more soluble in hot water especially in the presence of a trace of potassium hydroxide. It is very soluble in methyl alcohol and benzene. (Hg). It softens at 114° and melts at 117°.

Chloromercuri dimethyl-p-toluidine.

The acetate is treated with calcium chloride in alcohol. The chloride forms fine needles which are little soluble in alcohol, soluble in

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[114] Reitzenstein and Stamm, loc. cit.

[115] Klein, *Ber.* 11 (1878), 1743; 13 (1880), 835. Leeds, *J. Am. Chem. Soc.* 3 (1881), 147. Werner, *Z. anorg. Chem.* 15 (1897), 20. Rây, *J. Chem. Soc.* 101 (1912), 619.

[116] Pesci, *Gazz. chim. ital.* 28 II (1898), 103. *Chem. Zentr.* 1898 II 546. *Z. anorg. Chem.* 17 (1898), 277.

benzene, insoluble in water. (Hg). M.P. 159°. The *bromide* and *iodide* resemble the chloride. Their melting points are 149-50° and 126° respectively. The corresponding *nitrate* is made from the acetate by alcoholic calcium nitrate solution. It forms colorless needles which are soluble in hot benzene and alcohol. (Hg). M.P. 131°.

Mercuribis-(dimethyl-p-toluidine).

The hydroxide is treated with sodium thiosulfate solution in the usual way. The clear solution soon deposits a white precipitate. It is soluble in benzene and hot alcohol. (Mg,Mol.Wt.) It reacts with alcoholic solutions of the mercuric halides and mercuric acetate giving the corresponding RHg — salts.

Another preparation for this substance is from bromo-dimethyl-p-toluidine and ethyl acetate and 1.5 per cent sodium amalgam. This preparation proves that the mercury in the derivatives of dimethyl-p-toluidine is ortho to the dimethylamino group.

It is stated that acetoxymercuri dimethyl-p-toluidine dissolves in ammonium hydroxide and forms the R_2Hg compound slowly on standing.[117] This reaction is not mentioned in Pesci's later summaries of his work and is without parallel in the reactions of organic mercury compounds.

Mercury Derivatives of the Acid Toluidides.

N — Hg Compounds.

N-Mercuribis-(form-p-toluidide),

$$[CH_3 - C_6H_4 - N(CHO) -]_2Hg.$$ [118]

Formyltoluidine is treated with mercuric bromide and sodium ethylate. The mixture is precipitated by water. (Hg). It reacts with benzoyl chloride forming N-chloromercuri form-p-toluidide and the mixed diacylated toluidine.

C — Hg Compounds.

Derivatives of o-Acetotoluidide.[119]

p-Acetoxymercuri-o-acetotoluidide.

o-Acetotoluidide is refluxed with mercuric acetate in water. The reaction is complete in forty minutes. Crystals appear on standing.

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[117] Pesci, *Gazz.* 28 II (1898), 106. *Chem. Zentr.* 1898 II 546.
[118] Wheeler and McFarland, *Am. Chem. J.* 18 (1896), 545.
[119] Schoeller, Schrauth, and Rother, loc. cit. 2813.

Yield 28 per cent. The acetate is recrystallized from 80 per cent. alcohol. (CHHg). M.P. 228° (corr. 233°). When treated with iodine it yields p-iodo-o-acetotoluidide. M.P. 167.5°.

p-Chloromercuri-o-acetotoluidide.

The corresponding chloromercuri-o-toluidine is boiled with acetic anhydride. On cooling crystals separate which are easily soluble in absolute alcohol. (Hg). M.P. 167°.

o, p-Diacetoxymercuri-o-acetotoluidide.

The diacetoxymercuri compound of o-toluidine is treated with ethyl acetate and acetic anhydride. Fine crystals separate which are insoluble in common solvents, fairly soluble in hot water, very soluble in dilute acids, ammonium hydroxide and amines. (CHNHg). M.P. about 235°. Treatment with iodine gives a diiodide of the formula $C_9H_9ONI_2$, melting at 217.5° (corr. 222.5°).

Dichloromercuri-o-acetotoluidide.

The diacetate is treated with a chloride solution. (ClHg). The *bromide* and *iodide* have also been prepared.

Derivatives of m-Acetotoluidide.[120]

Acetoxymercuri-m-acetotoluidide.

The toluidide is refluxed with less than one molecule of mercuric acetate in water. No mercuric ions are left after one hour. Yield 20 per cent. The product is purified by recrystallization from 30 per cent alcohol. (CHHg). M.P. 99°. The original mother liquor when treated with a chloride solution gives a precipitate of the corresponding *chloride.*

Diacetoxymercuri-m-acetotoluidide.

The corresponding diacetoxymercuri-m-toluidine is treated with acetic anhydride. It is insoluble in common solvents, slightly soluble in hot water, very soluble in ammonium hydroxide. (Hg). When treated with iodine it forms diiodo-m-acetotoluidide melting at 209° (corr. 214°).

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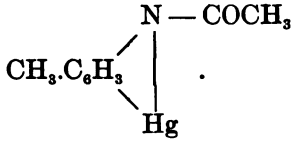
[120] Schoeller, Schrauth, and Rother, loc. cit. 2814.

Triacetoxymercuri-m-acetotoluidide.

The corresponding trimercurated m-toluidine is heated with acetic anhydride. The product is insoluble in organic solvents, soluble in ammonium hydroxide, and very soluble in water even in the cold. (CHHg). Ammonium sulfide gives no action until boiled.

Derivatives of p-Acetotoluidide.

Anhydride of o-hydroxymercuri-p-acetotoluidide,



$$CH_3.C_6H_3\left<\begin{array}{l}N-COCH_3\\ \;|\\ Hg\end{array}\right. .$$

The toluidide is boiled with aqueous mercuric acetate. The product forms leaflets. (Hg). M.P. 224° (corr. 229°). The loss of acetic acid between the acetamino group and the ortho hydroxymercuri group apparently takes place only on boiling. None of the analogous derivatives of o- and m-acetotoluidide show this loss of acetic acid. It happens that none of these compounds having these groups in the *ortho* position is made in boiling water solution. In each case the preparation has been from the mercurated toluidine and acetic anhydride.

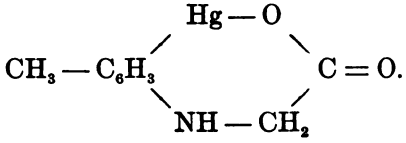
Mercury Derivatives of the Toluidoacetic Acids.

o′(?)-acetoxymercuri-o-tolylglycine ethyl ester,

$$AcOHg-C_6H_3(CH_3)-NH.CH_2CO_2C_2H_5.$$

Equal molecules of the toluido ester and mercuric acetate are allowed to react in methyl alcohol. Yield 77 per cent. The product is soluble in methyl and ethyl alcohols, ethyl acetate, chloroform, acetone, insoluble in low boiling ligroin. It is soluble in ammonium hydroxide and in dilute acids. It is best recrystallized from ethyl acetate. (CHHg). M.P. 122°. Saponification and acidification give the anhydride.

Anhydride of o′(?)-hydroxymercuri-o-tolylglycine,



$$CH_3-C_6H_3\left<\begin{array}{c}Hg-O\\ \\ NH-CH_2\end{array}\right>C=O.$$

The ester is warmed with 2 molecules of sodium hydroxide, cooled, and treated with 1 equivalent of normal sulfuric acid. Yield 93 per cent. The anhydride is insoluble in water and organic solvents but dissolves readily in alkalies. (CHHg).

Diacetoxymercuri-o-tolylglycine ethyl ester.

The toluido ester is treated with two molecules of mercuric acetate in methyl alcohol. Yield 83 per cent. It is insoluble in ethyl acetate, difficultly soluble in hot alcohol, very soluble in ammonium hydroxide, and saponified by hot alkalies. (CHHg). M.P. 164° (corr. 167°).

o(?)-acetoxymercuri-m-tolylglycine ethyl ester.

Equivalent amounts of the toluido ester and mercuric acetate are allowed to react in dilute methyl alcohol. Yield 63 per cent. It is purified by dissolving in ethyl acetate and precipitating by low boiling ligroin. (CHHg). M.P. 127°. Saponification and acidification yield a yellow *anhydride*. (CHHg).

Triacetoxymercuri-m-tolylglycine ethyl ester.

m-Toluidoacetic ethyl ester is treated with three molecules of mercuric acetate in methyl alcohol. Yield 20 per cent. The rest of the material can be recovered from the mother liquors as the less soluble *chloride*. The acetate is difficultly soluble in methyl and ethyl alcohols, easily soluble in ammonium hydroxide, insoluble in most common solvents. (CHHg). M.P. about 182°. No di-mercurated compound can be obtained from m-toluidoacetic ester in methyl alcohol. When only two molecules of mercuric acetate are used the product is an oily substance which may be a mixture of mono- and di-mercurated esters.

o-Acetoxymercuri-p-tolylglycine ethyl ester.

The preparation in the usual way gives an 80 per cent yield. The properties of the product resemble those of the corresponding monomercury derivatives of the o- and m-toluidoacetic esters. (CHHg). M.P. 139°. Saponification and acidification gives the *anhydride* which forms a white amorphous precipitate. (CHHg).

p-Bromoaniline reacts with mercuric acetate giving a series of complex mercury compounds similar to those obtained from p-aminobenzoic ester.[121]

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[121] Unpublished results, Whitmore and V. E. Meharg. Cf. Schoeller, Schrauth, and Liese, *Ber.* 52 (1919), 1782.

Mercury Derivatives of Benzylamine.[122]

Benzylamine and related compounds give two types of mercury compounds neither of which contains the C — Hg linkage. The first type consists of "addition compounds" made up of one molecule of the mercuric salt and one molecule of the amine. Such compounds are obtained from benzylamine, benzyl methyl amine, and benzyl ethyl amine. Conductivity measurements indicate that these are pentavalent nitrogen derivatives like $C_6H_5CH_2 — NH_2Cl — HgCl$. The second type of compound may be obtained by boiling the mercuric salt with an excess of the amine. $C_6H_5CH_2 — NH — HgCl$ and the corresponding acetate have been described. (CHNClHg). The existence of such a compound is of interest in supporting Franklin's theory of ammonobasic salts.

Mercury Derivatives of Benzylaniline.[123]

p-Benzylaminophenylmercuric acetate,

$$C_6H_5CH_2 — NHC_6H_4 — HgOAc.$$

Equivalent amounts of benzylaniline and mercuric acetate in 50 per cent alcohol are allowed to react at 50°. The product is crystallized from hot benzene. It forms tufted needles which are insoluble in water, slightly soluble in cold alcohol, fairly soluble hot, easily soluble in chloroform. (CHHg). M.P. 144°.

p-Benzylaminophenylmercuric hydroxide.

The powdered acetate is treated with concentrated potassium hydroxide forming a crystalline powder made up of small colorless prisms. It is slightly alkaline to "sunflower extract" but not to phenolphthalein. It dissolves slightly in hot water with decomposition. It is decomposed by benzene, and methyl and ethyl alcohols. It starts to soften at 82.5° and melts at 215° with decomposition. It contains 1.5 molecules of water of crystallization. (Hg,H_2O).

The hydroxide heated with sodium thiosulfate solution forms p-mercuribis-benzylaniline.

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[122] André, *Compt. rend.* 112 (1891), 997. Pesci, *Gazz. chim. ital.* 26 II (1896), 54. *Chem. Zentr.* 1896 II 630. *Z. anorg. Chem.* 15 (1897), 221. Prussia, *Gazz. chim. ital.* 27 I (1897), 15. Franklin, *J. Am. Chem. Soc.* 29 (1907), 43. Rây and Dhar, *J. Chem. Soc.* 103 (1913), 4.

[123] Prussia, loc. cit. Pesci, loc. cit.

p-Benzylaminophenylmercuric chloride.

The acetate is treated with calcium chloride in alcohol. It forms a white crystalline powder which is slightly soluble in hot benzene, soluble in hot methyl and ethyl alcohols, insoluble in water. (Hg). M.P. 173-4°. The corresponding *nitrate* is prepared from the hydroxide and a very slight excess of 20 per cent nitric acid. It forms a white crystalline powder which is decomposed by hot water and is insoluble in methyl and ethyl alcohols, slightly soluble hot, insoluble in benzene. (Hg). M.P. 150° decomp.

p-Mercuribis-benzylaniline, $Hg(C_6H_4 — NH — CH_2 — C_6H_5)_2$.

A suspension of the hydroxide in water is treated with an excess of 25 per cent sodium thiosulfate solution. The product crystallizes from hot benzene in small colorless needles. It is insoluble in methyl and ethyl alcohols. (Hg, low). M.P. 171.5° with partial decomposition. During its formation one equivalent of sodium hydroxide is formed for each molecule of the complex hydroxide used.

Mercury Derivatives of Miscellaneous Aromatic Amines.

The *xylidines* react with mercuric acetate.[124]

Various *aminoarylsulfonic acids* have been treated with mercuric salts.[125]

Acetoxymercuri sulfanilic acid is obtained as a white amorphous solid on warming sulfanilic acid with mercuric acetate in water solution.[125a] It is soluble in dilute alkalies and acids.

Aminoarylarsonic acids react with mercuric compounds.[126]

Mercury Derivatives of the Naphthylamines.

N-Mercury Compounds.[127]

When the acylated α-naphthylamines are treated with mercuric chloride and sodium carbonate N — Hg compounds are obtained. The formyl and acetyl derivatives have been treated in this way. The product reacts with sodium thiosulfate, potassium iodide, and am-

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[124] J. Rother, *Dissert.* Berlin 1911, p. 58.

[125] D. R. P. 281,009. *Chem. Zentr.* 1915 I 73.

[125a] Private communication, G. W. Raiziss.

[126] *Chem. Zentr.* 1909 II 1817. D. R. P. 239,557. *Chem. Zentr.* 1911 II 1398. D. R. P. 272,289. *Chem. Zentr.* 1914 I 1469.

[127] Wheeler and McFarland, *Am. Chem. J.* 18 (1896), 547. Prussia, *Gazz. chim. ital.* 28 II (1898), 127. *Chem. Zentr.* 1898 II 928.

monium bromide in the way N — Hg compounds usually do, forming the original — NH — compound and a molecule of inorganic base for each N — Hg linkage broken.

Addition compounds of the naphthylamines have been obtained by treating them with mercuric salts in alcohol solution.[128]

C-Mercury Compounds.

2, 4-Diacetoxymercuri-α-naphthylamine.[129]

No monomercury compound is obtainable. A solution of α-naphthylamine in alcohol and acetic acid is treated with one or two molecules of mercuric acetate. An intense yellow precipitate is first formed. This soon changes to a mass of white crystals. Yield 95 per cent. Sodium hydroxide gives a slight yellow color but ammonium sulfide gives no action even on long standing. (Hg, low, HOAc, high). The C — Hg linkage is slightly split by boiling with potassium iodide solution. The amount of potassium hydroxide is only 5 per cent of what would be formed by complete splitting of both C — Hg linkages. When the mercury compound is treated with potassium iodide and then with ammonium sulfide a distinct blackening is observed. This is further evidence of the splitting effect of potassium iodide on some C — Hg linkages.

1-Acetoxymercuri-β-naphthylamine.

Equivalent amounts of β-naphthylamine and mercuric acetate are mixed in acetic acid. The colorless solution soon deposits colorless crystals. These are soluble in water containing a trace of alkali. Concentrated alkali turns the compound yellow and ammonium sulfide readily forms mercuric sulfide. This is in sharp contrast to the behaviour of the dimercurated alpha compound. Halogen salts give very little alkali, indicating that the splitting of the C — Hg is comparatively slight. (Hg, low, HOAc, high).

Mercury Derivatives of Naphthylamine Sulfonic Acids.

Derivatives of Naphthionic Acid.

(α-Naphthylamine-4-sulfonic acid.)[130]

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[128] Zinin, *J. prakt. Chem.* (1) 27 (1842), 148. Klein, *Ber.* 11 (1878), 1743. Leeds, *J. Am. Chem. Soc.* 3 (1881), 150. Lachowicz and Bandrowski, *Monatsh.* 9 (1888), 515. Lachowicz, *Monatsh.* 10 (1889), 893.

[129] Brieger and Schulemann, *J. prakt Chem.* (2) 89 (1914), 141.

[130] *Ibid.* 151 ff.

2-Acetoxymercuri naphthionic acid.

A cold solution of the sodium salt of naphthionic acid is treated with mercuric acetate forming a fine white precipitate. Boiling this precipitate gives a compound which is soluble in acetic acid. When the acetic acid solution is cooled, colorless crystals separate. These are soluble in sodium hydroxide with only a little blackening. No mercuric oxide is formed. Ammonium sulfide does not act at first but in a little while gives mercuric sulfide. (Hg).

The structure given seems more likely than that suggested by Brieger and Schulemann who regard the compound as an internal salt with the mercury attached to the sulfonic acid and a molecule of acetic acid added to the amino group.[131]

Sodium salt of 2-Hydroxymercuri naphthionic acid.

The acetate is treated with a large excess of sodium hydroxide. White needles of the sodium salt separate. (NaHg). The sodium salt does not react with ammonium sulfide. When it stands in a vacuum over phosphorus pentoxide it changes to a canary yellow compound. This may be due to the elimination of water between the amino group and the ortho hydroxymercuri group giving an anhydride similar to that obtained with mercurated toluidine.

No dimercurated naphthionic acid has been obtained. When an excess of mercuric acetate is used yellow solutions are obtained which give a yellow red color with sodium hydroxide.

Derivatives of 1, 5-Naphthylamine Sulfonic Acid.

Diacetoxymercuri-1, 5-naphthylamine sulfonic acid.

No monomercurated product has been obtained. A solution of the sodium salt of the acid is barely acidified with dilute acetic acid and a water solution of two molecules of mercuric acetate is added. The fine canary yellow precipitate is soluble in hot acetic acid. Sodium hydroxide dissolves it without forming any mercuric oxide. This alkaline solution on standing deposits mercurous oxide. The mercury compound gives no action with ammonium sulfide. (Hg,HOAc). It is, however, very sensitive to halide salts. Potassium iodide gives a quantitative splitting of the C — Hg linkage. Although the mercury

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[131] Their article (p. 152) contains a typographical error as this substance is formulated as a derivative of β-naphthylamine.

compound alone does not blacken with ammonium sulfide it does so at once when sodium chloride is added. It is remarkable that the C — Hg linkage in this case is more easily broken by sodium chloride than it is by a sulfide.

Derivatives of 2, 6-Naphthylamine Sulfonic Acid.

Only a monomercurated compound has been obtained. The sodium salt reacts with mercuric acetate in the cold, giving a compound from which sodium hydroxide precipitates mercuric oxide. If the mixture is heated a product is obtained which does not react with sodium hydroxide but does react readily with ammonium sulfide. The formation of a monomercurated product which reacts at once with ammonium sulfide is the same as with α-naphthylamine itself. The product is insoluble in all solvents. The analyses for mercury, nitrogen, and acetic acid indicate that the substance is a mixture of several compounds, probably the acetate and the internal salts formed between the sulfonic acid group and the amino group, and between the sulfonic acid group and the hydroxymercuri group. The mercury is undoubtedly in the alpha position next to the amino group.

Sodium salt of 1-Hydroxymercuri-2, 6-naphthylamine sulfonic acid.

The above impure product is treated with an excess of sodium hydroxide. The product is colorless. It is soluble in water, dilute alcohol, and dilute alkalies. It contains one molecule of water which cannot be removed in a vacuum over phosphorus pentoxide. (CHS NaHg).

The hydroxide does not react with ammonium sulfide. If, however, it is treated with diazotized sulfanilic acid the solution immediately reacts with ammonium sulfide. This indicates that the mercury has been removed from the ring during the coupling reaction. As the coupling normally takes place in the alpha position next to the amino group, that is probably the position occupied by the mercury.

When the monoethyl and dimethyl derivatives of 2, 6-naphthylamine sulfonic acid are treated with mercuric acetate the latter is reduced. No product is obtained which does not act at once with ammonium sulfide.

2, 4-Naphthylamine sulfonic acid reacts with mercuric acetate in water solution forming a compound which is believed to be *5-acetoxymercuri-2, 4-naphthylamine sulfonic acid.*[132]

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[132] Private communication, G. W. Raiziss.

Chapter XI.

Mercury Derivatives of Phenols, Naphthols, and Related Compounds.

Mercury Derivatives of Phenol.[1]

The compounds formerly regarded as O — Hg compounds of phenols are in reality C — Hg compounds. The former compounds are apparently formed at first, but quickly change to the more stable form. Thus the mixing of solutions of potassium phenolate and mercuric chloride gives a brick red precipitate which soon turns yellow and on standing 48 hours becomes entirely colorless. The first precipitate is perhaps a compound with the grouping O — HgCl while the latter is undoubtedly p-chloromercuri phenol.

Mercuric salts of oxygen acids react readily with phenol. The reaction is complete in less than half an hour as shown by the fact that sodium hydroxide no longer gives HgO with a sample of the mixture. Mercuric chloride reacts with phenol only to the extent of 2 per cent in four days. In the presence of sodium acetate it reacts about 40 per cent in the same length of time.

Mercuric oxide reacts with sodium phenolate, giving a white alkali insoluble compound.[2] Phenol treated with mercuric acetate solution gives a mixture of the o- and p- monomercurated compounds and the o- p- di-mercurated compound. The mixture is hard to separate. Similar products are obtained from sodium phenolate treated with an alcoholic solution of mercuric chloride. The "hydrargyrum carbolicum" of the pharmacists is really a mixture of the hydroxides of these three compounds.

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[1] Desesquelle, *Bull. soc. chim.* (3) 11 (1894), 266. Dimroth, *Ber.* 31 (1898), 2155; 32 (1899), 761. *Chem. Zentr.* 1901 I 451. *Ber.* 35 (1902), 2033, 2853. Hofmann, *Ber.* 38 (1905), 2002.

[2] Dimroth, *Ber.* 31 (1898), 2155.

o-Chloromercuriphenol.[3]

Preparation and Properties.

The ortho compound is obtained from its mixture with the para or with the p- and o, p- compounds by extraction with cold alcohol in which the others are practically insoluble. The mixture of the chlorides may be obtained in two ways. Mercuric acetate reacts even with a large excess of phenol giving all three products. If the reaction between mercuric acetate and an excess of phenol is carried out by heating without a solvent the product consists of a mixture of the two monomercurated phenols.[4] The o-chloride can be crystallized from hot water. M.P. 152.5° (CHHg). It is soluble in sodium hydroxide. The treatment of this solution with alcohol precipitates a crystalline sodium salt.

Reactions.

1. Benzoylation by the Schotten-Baumann reaction gives a *compound,* $ClHg—C_6H_4OCOC_6H_5$, which crystallizes from much alcohol in fine needles. M.P. 204° (CHHg).

Gentle warming with acetyl chloride gives an 80 per cent. yield of an acetyl derivative melting at 170-1° (Hg).[5]

2. Acid reducing agents, like dilute stannous chloride, give metallic mercury and phenol.

3. Dilute acids readily split the C — Hg bond, giving mercuric salts and phenol.

4. Alkylation of the sodium derivative by ethyl iodide gives a mixture of o-phenetylmercuric iodide and a considerable amount of mercury diphenetyl. The formation of the latter is probably due to the effect of the inorganic iodide formed in the reaction.[6]

5. Coupling with diazonium salt solutions.[7]

An alkaline solution of the mercurated phenol reacts with benzene diazonium chloride solution giving p-benzeneazo-o-chloromercuriphenol. This forms a yellow hydrate which melts at about 125°. The dehydrated substance is red and melts at 147°. The anhydrous substance prepared in a vacuum is very hygroscopic while that prepared at a high temperature is not. The substance forms a compound with

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[3] Dimroth, *Ber.* 31 (1898), 2155; 32 (1899), 762. *Chem. Zentr.* 1901 I 451.

[4] Whitmore and Middleton, *J. Am. Chem. Soc.* 43 (1921), 622.

[5] *Ibid.*

[6] Dimroth, *Ber.* 32 (1899), 763.

[7] Dimroth, *Chem. Zentr.* 1901 I 451. *Ber.* 35 (1902), 2853. Reitzenstein and Bönitsch, *J. prakt. Chem.* (2) 86 (1912), 80.

one molecule of acetic acid. (NClHg,HOAc). It also gives an addition compound with one molecule of hydrochloric acid. This molecule of acid is lost only on boiling with water.

An alkaline solution of the phenol can also be coupled with the diazonium product from m-amino leucomalachite green. The product is a dark green precipitate which turns dark brown on drying.

6. *Reaction with nitrous acid. p-Nitroso-chloromercuriphenol.*[8]

An alkaline solution of the o-mercurated phenol is treated with sodium nitrite and acidified with sulfuric acid at —5°. The product recrystallizes from xylene or anisole in light brown needles. (NCl). It is partly soluble in ether with a green color. It reacts with a mixture of ammonium chloride, acetate, and carbonate forming *p-nitroso-o-chloromercuri aniline.*

7. An alkaline solution of the anhydride of o-hydroxymercuri phenol when treated with carbon dioxide gives a precipitate of an inner anhydride of o-hydroxymercuriphenol. This is insoluble in all organic solvents except phenol. (CHHg,MW in phenol).[9]

Similar compounds have been observed in other cases where the —HgOAc group is ortho to the —OH group, as in the case of Triacetoxymercuriphenolphthalein which loses acetic acid at 120° forming such an anhydride.[10]

8. With inorganic halides.[11]

Boiling with an excess of aqueous potassium iodide gives phenol, inorganic mercury compounds, and almost exactly one molecule of alkali. This easy splitting of the C — Hg linkage in the mercurated phenol is in sharp contrast to the behaviour of the corresponding acetylated compound which reacts with potassium iodide giving the R_2Hg compound, mercury di(o-acetoxyphenyl), $(CH_3CO-OC_6H_4)_2Hg$.

9. With potassium sulfocyanate.[12]

Boiling with potassium sulfocyanate gives an alkaline solution and a strong odor of phenol. Apparently potassium sulfocyanate has the same splitting effect on the C — Hg linkage as potassium iodide. The similarity of the action of the two reagents is complete as the sulfocyanate also reacts with the acetylated compound giving mercury di(o-acetoxyphenyl).

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[8] Kharasch and Piccard, *J. Am. Chem. Soc.* 42 (1920), 1860.

[9] D. R. P. 272,607. Fränkel, 671. Brit. Pat. 24,981. *Chem. Abst.* 6 (1912), 1547.

[10] White, *J. Am. Chem. Soc.* 42 (1920), 2363.

[11] Whitmore and Middleton, loc. cit.

[12] Unpublished results, Whitmore and Middleton.

p-Acetoxymercuri phenol.[13]

Mercuric chloride acting on eight moles of potassium phenolate gives a precipitate which was formerly regarded as basic mercuric phenolate but is probably a C — Hg compound. When this is treated with acetic acid, colorless prisms are obtained which melt with decomposition at a high temperature. The substance is very little soluble in water and alcohol. (HgCH).

A compound which may be the same as that just mentioned is obtained by adding more mercuric acetate to the precipitate obtained from the sodium phenolate and mercuric acetate. It is described as consisting of crystals melting at 149°.

p-Chloromercuriphenol.[14]

Preparation and Properties.

1. From the mother liquor from the di-acetoxymercuriphenol treated with sodium chloride solution. The resulting precipitate is extracted with cold alcohol to remove any of the ortho chloride.
2. The mixture of the ortho and para acetates, obtained by fusing mercuric acetate with an excess of phenol, is dissolved in hot alcohol and precipitated by sodium chloride solution. The p-chloride precipitates even hot and is filtered off at once leaving the ortho compound in the mother liquor.[15] It is recrystallized from acetone or alcohol. Fine needles. M.P. 219-220° (224-5°) (CHHg). It is soluble in alkali.
3. Five per cent phenol solution in water is heated with alum, zinc sulfate, and mercuric chloride. The solution on standing deposits crystals melting at 210°.
4. A solution of potassium phenolate treated with mercuric chloride solution at 35-40° gives a brick red precipitate which turns yellow and then white on standing for 48 hours. Extraction with hot alcohol gives colorless crystals which melt about 210° with decomposition. (CHClHg).

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[13] Desesquelle, *Bull. soc. chim.* (3) 11 (1894), 268.

[14] Desesquelle, loc. cit. Dimroth, *Ber.* 31 (1898), 2155; 32 (1899), 761. Grützner, *Arch. Pharm.* 236 (1899), 622. *Chem. Zentr.* 1899 I 203. Dimroth, *Chem. Zentr.* 1901 I 452. *Ber.* 35 (1902), 2862. Brit. Pat. 24,981. *Chem. Abst.* 6 (1912), 1547.

[15] Whitmore and Middleton, loc. cit.

Reactions.

1. The Schotten-Baumann reaction gives a *benzoyl derivative* which crystallizes from ethyl benzoate in leaflets. M.P. 275-6° (CHHg).[16]

Treatment with acetyl chloride gives an *acetyl derivative* which melts at 235° (Hg).[17]

2. With diazonium salts.[18]

An alkaline solution of the chloride reacts with benzene diazonium chloride forming hydroxyazobenzene, mercuric oxide, and a small amount of *o-benzeneazo-p-chloromercuriphenol.* The latter substance forms yellow masses containing acetic acid. Dried at 100° it turns red. M.P. 130-1° (CHHg). Most of the mercury in the position in which coupling usually takes place is split out as inorganic mercury.

3. With inorganic halides.[19]

Boiling with potassium iodide solution removes the mercury quantitatively forming phenol, potassium hydroxide, and potassium mercuric iodide. The corresponding acetylated compound does not lose mercury when treated in this way but is only changed to the organomercuric iodide, $CH_3CO — OC_6H_4HgI$.

Miscellaneous work on p-chloromercuriphenol.[20]

p-Hydroxymercuriphenol.[21]

The white precipitate formed from mercuric chloride and an excess of potassium phenolate probably has this structure. It can be crystallized from a hot concentrated phenol solution. (HgCH).

The oxide corresponding to this hydroxide, $(HO — C_6H_4 — Hg)_2O$, is obtained by dissolving the chloride in sodium hydroxide and precipitating by carbon dioxide. Extraction with acetone removes impurities. It decomposes slowly at 180°. It is insoluble in all organic solvents except boiling phenol from which alcohol causes it to separate as a crystalline powder. Apparently the internal anhydride cannot exist as it does with the corresponding ortho compound.[22]

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[16] Dimroth, *Ber.* 32 (1899), 761.

[17] Whitmore and Middleton, loc. cit.

[18] Dimroth, *Chem. Zentr.* 1901 I 451. *Ber.* 35 (1902), 2853.

[19] Whitmore and Middleton, loc. cit.

[20] Brit. Pat. 24981 loc. cit. , Fränkel, *Die Arzneimittelsynthese,* 4th Ed. 1919, p. 671.

[21] Desesquelle, loc. cit. *Realenzyk. Pharm.* VI 500. Schmidt, *Pharmazeutische Chemie,* II 1076.

[22] Dimroth, *Chem. Zentr.* 1901 I 450. *Ber.* 35 (1902), 2854.

Di-mercurated Compounds of Phenol.[23]

Di-acetoxymercuri phenol.

An aqueous solution of phenol and two moles of mercuric acetate is heated on the steam bath. M.P. 216-7° (CHHg).

Reactions.

1. Iodine reacts with the di-acetate in acetic acid forming di-iodophenol. The action with iodine is quantitative and the reaction can be used as a method of analyzing mercurated phenols by iodimetry.[24]

2. With diazonium salt solutions.

Benzene diazonium chloride reacts with the di-acetate dissolved in dilute sodium hydroxide giving *p-benzeneazo-o-acetoxymercuriphenol* in the alkaline solution and an insoluble residue of mercuric oxide and *o-benzeneazo-o, p-diacetoxymercuriphenol.* The latter is obtained as the chloride by dissolving the residue with warm dilute sodium hydroxide, precipitating by carbon dioxide, dissolving in acetic acid and precipitating by sodium chloride.

3. With inorganic halides.[25]

Boiling with aqueous potassium iodide splits the C — Hg linkage quantitatively giving phenol, potassium mercuric iodide, and almost exactly two equivalents of base.

p-Benzeneazo-o-acetoxymercuri-phenol. Yellow powder. M.P. 197-8° (CHHg).

Sodium chloride gives the corresponding *chloride.* o-Benzeneazo-o, p-dichloromercuriphenol precipitated by sodium chloride from acetic acid solution contains one molecule of acetic acid. It forms a red brown powder. M.P. 165-70° decomp. It loses acetic acid at 110° or on boiling with water. (CHHg,HOAc).

The sodium salt of *o, p-dihydroxymercuriphenol* is known as "Providol." [26]

o, p-Dichloromercuriphenol.[27]

If the product from the mercuration of phenol in solution is treated with sodium chloride and the resulting precipitate is extracted with

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[23] Dimroth, *Ber.* 31 (1898), 2154; 32 (1899), 763; 35 (1902), 2863. *Chem. Zentr.* 1901 I 452. Brieger, *Arch. Pharm.* 250 (1912), 62. *Chem. Zentr.* 1912 I 753. *Brit. Pat.* 24,981 loc. cit.

[24] Brieger, loc. cit.

[25] Whitmore and Middleton, loc. cit.

[26] Fränkel, loc. cit. 659.

[27] Dimroth, *Ber.* 32 (1899), 763.

boiling alcohol, the residue is the di-chloride compound. White powder, almost insoluble in all solvents. Decomposes at 258° without melting. (CHHg). The *benzoyl compound* is prepared in the usual way. It is a white powder insoluble even in ethyl benzoate. (CH).

Mercuribis-phenol Compounds.

Mercuribis-o-phenol.[28]

If the ortho chloride is treated with sodium thiosulfate a clear solution is first obtained. In a few seconds this becomes cloudy. The white powder formed can be crystallized in small amounts from hot alcohol. The recrystallization must be carried out as rapidly as possible to avoid decomposition. The product forms white tablets, rather easily soluble in alcohol, acetic acid, and acetone, almost insoluble in water, ether, and chloroform even on boiling. Heating causes it to turn gray without melting. The alcohol solution on boiling for a few minutes turns brown and deposits metallic mercury. It is easily soluble in sodium hydroxide, insoluble in sodium carbonate, precipitated by carbon dioxide from alkaline solution. (CHHg).

Mercuribis-o-phenylacetate, $Hg(C_6H_4O — COCH_3)_2$.[29]

Preparation.

1. The acetyl derivative of o-hydroxyphenylmercuric chloride boiled with potassium iodide solution gives a 20 per cent yield of R_2Hg.
2. The acetyl derivative of o-hydroxyphenylmercuric chloride dissolves readily in sodium thiosulfate solution. On standing three days an 80 per cent yield of R_2Hg separates.

Properties.

It forms white needle crystals which melt at 125°. It is slightly soluble, on heating, in alcohol, benzene, and chloroform. It is only difficultly soluble in ether. (Hg).

Reactions.

1. With inorganic halides.

Boiling with an excess of potassium iodide produces no change. The stability of the C — Hg linkage is evidently increased by the acetylation of the phenolic hydroxyl.

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[28] Dimroth, *Ber.* 35 (1902), 2855. *Chem. Zentr.* 1901 I 449-54.

[29] Whitmore and Middleton,. *J. Am. Chem. Soc.* 43 (1921), 619.

2. With mercuric chloride.

The usual reaction of R_2Hg compounds takes place forming o-acetoxyphenylmercuric chloride melting at 170°.

3. With bases.

Sodium hydroxide not only saponifies the acetoxy groups but breaks one of the C — Hg linkages. This change of R_2Hg to RHgX by means of a base is very unusual.[30] Boiling with 5 per cent sodium hydroxide and neutralizing with acetic acid gives a white amorphous substance which appears to be $(HO — C_6H_4 — Hg)_2O$. (Hg). It is thus analogous to the compound obtained in the para series,[31] by dissolving RHgCl in sodium hydroxide and precipitating by carbon dioxide.

4. With acids.

Concentrated hydrochloric acid has little action except on heating or standing for some time. This is evidenced by the fact that a suspension of the mercury compound in the acid does not react with hydrogen sulfide unless heated or allowed to stand at least an hour.

5. With sulfides.

No reaction takes place with ammonium sulfide in less than three days. Then a slight red precipitate separates.

Mercuribis-p-phenylacetate.

The preparation and properties of this substance resemble those of the ortho compound. It is, however, harder to bring about the change to R_2Hg than in the ortho series. Treatment of p-acetoxyphenylmercuric chloride with an excess of potassium iodide produces no change but the formation of the organomercuric iodide. No R_2Hg can be obtained in this way. The reaction with sodium thiosulfate gives the desired compound. The yield is only 50 per cent as compared with that of 80 per cent obtained in the preparation of the ortho compound. The product melts 172-3°. Its solubilities resemble those of the ortho compound. It reacts with mercuric chloride, sodium hydroxide, acids, and sulfides in the same way as its isomer.

Reaction of Phenol Ethers with Mercuric Compounds.

Phenol ethers react much less readily with mercuric acetate than do the free phenols. They must be heated on the water bath and

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[30] Whitmore and Middleton, *ibid.* 624. Stieglitz, Kharasch, and Hanke, *J. Am. Chem. Soc.* 43 (1921), 1185.

[31] Dimroth, *Ber.* 35 (1902), 2854.

even then only one mercury atom is introduced into the ring.[32] Manchot believes that an "addition" compound is formed first and then rearranges in such a way that the mercury replaces a ring hydrogen.

Derivatives of Anisole.

o-Mercury Dianisyl.[33]

Preparation.

1. From o-bromanisole and 1.5 per cent sodium amalgam in the usual way.
2. From o-iodomercurianisole and sodium stannite solution.
3. From o-iodomercurianisole and potassium iodide solution.[34]

Properties and Reactions.

It crystallizes in monoclinic prisms which are easily soluble in benzene, chloroform, and less soluble in hot alcohol. M.P. 108°. It reacts with mercuric salts and with acids in the usual way forming salts of the type R — Hg — X.

o-Acetoxymercuri anisole.

Prepared from the dianisyl compound dissolved in hot acetic acid and precipitated by water. When recrystallized from alcohol, it forms fine needles. M.P. 123-4° (CH).

o-Halidemercuri anisoles.

These may be prepared by the usual reaction of the R_2Hg compound with mercuric halides in alcohol. They are more soluble in alcohol than the corresponding p- compounds. *Chloride.* It is also prepared by adding sodium chloride solution to the mother liquors from the preparation of the p-acetate from mercuric acetate heated with an excess of anisole.[35]

When the mixture is treated with steam, the o-chloromercuri compound passes over with the unchanged anisole leaving the p-compound behind. The chloride is crystallized from alcohol in fine needles, from chloroform in small tablets. It is difficultly soluble in cold benzene,

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[32] Dimroth, *Ber.* 35 (1902), 2867. Manchot, *Ann.* 421 (1920), 333.

[33] Michaelis, *Ber.* 27 (1894), 257. Dimroth, *Ber.* 35 (1902), 2853.

[34] Unpublished results, Whitmore and Middleton.

[35] Dimroth, loc. cit. 2867.

more easily in hot benzene and chloroform. M.P. 173-4°[36] (Cl). *Bromide* M.P. 183° (Br). *Iodide.* It can also be prepared from the chloride by treating with an iodide solution. It is also formed when an alkaline methyl alcohol solution of o-chloromercuriphenol is treated with methyl iodide.[37] Small colorless needles. M.P. 165° (I). It reacts with sodium stannite solution or potassium iodide forming o-mercury dianisyl.

p-Mercury Dianisyl.[38]

It can be prepared from p-bromanisole and sodium amalgam in the usual way. Fine white needles. M.P. 202°. It sublimes, on careful heating, at 200°. It is fairly soluble in cold benzene, easily in hot benzene, easily soluble in cold chloroform, less soluble in alcohol, insoluble in hydrochloric acid, but on long heating gives anisole and mercuric chloride. (CHHg). When heated with an excess of pure phosphorus trichloride at about 200° it gives mercuric chloride and $CH_3O — C_6H_4PCl_2$.

Reaction of Anisole with Mercuric Acetate.

1. In water solution.[39]

Addition compound of anisole and mercuric hydroxide.

The reaction at 50° is very slow. A white precipitate starts to form after several days. Even on long standing the solution still contains mercuric ions. The precipitate is filtered off and dried on a porous plate in a vacuum. M.P. 170°. Recrystallization from 25 per cent acetic acid gives fine needles melting at 173°. 7.8 gm. of anisole treated with three molecules of mercuric acetate gives 20 gm. of the precipitate. It gives no mercury reaction with sodium hydroxide, ammonium hydroxide, or ammonium sulfide. Hot dilute HCl gives anisole. The precipitate subjected to steam distillation gives no volatile product. If acidified with 20 per cent HCl and then steam distilled it gives anisole. It is fairly soluble in hot water and can be recrystallized from

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[36] A chloride melting 177-8° is obtained in the following manner: o-Hydroxyphenylmercuric chloride is treated with sodium hydroxide and methyl iodide forming o-anisylmercuric iodide. This reacts with potassium iodide giving o-mercury dianisyl, which in turn reacts with mercuric chloride giving o-anisylmercuric chloride melting at 177-8°. Unpublished results, Whitmore and Middleton.

[37] Dimroth, *Ber.* 31 (1898), 2155. *Chem. Zentr.* 1901 I 451.

[38] Michaelis, *Ann.* 293 (1896), 248. Michaelis and Rabinerson, *Ber.* 23 (1890), 2343.

[39] Manchot, *Ann.* 421 (1920), 334.

dilute alcohol. It is neutral to litmus. It contains no acetate, (cacodyl test). (CHHg). Analyses for C, H, and Hg agree with the formula, $(CH_3O — C_6H_5.HgOH)OH$, which is used to indicate that only one of the OH groups is replaceable by acid radicals. The substance seems to lose water. It might, therefore, be a true C — Hg compound containing one molecule of water. This idea receives some support from the fact that the hydroxide readily reacts with sodium chloride forming the p-chloromercurianisole of M.P. 237°. There is no doubt of the structure of the latter compound as it has been made from p-mercury dianisyl which in turn can be made from p-bromanisole.

2. Without solvent.[40] When anisole is heated with mercuric acetate an acetoxymercuri group is introduced into the p-position.

p-Acetoxymercuri anisole.

Dry mercuric acetate is heated with 8 molecules of anisole on a water bath until the reaction is complete (NaOH test). Cooling gives crystals which can be recrystallized from alcohol. M.P. 176.5° (CHHg). The mother liquor treated with sodium chloride gives some o-compound which can be removed by steam distillation along with the unchanged anisole.

The acetate can also be prepared by dissolving the mercury dianisyl compound in hot glacial acetic acid and cooling the solution to get crystals. It is somewhat soluble in hot water, from which it separates in fine needles. (CH).[41]

p-Propionoxymercuri anisole.[42]

p-Mercury dianisyl is dissolved in propionic acid and treated with sodium carbonate solution to neutralize the excess of acid. M.P. 105.5°.

p-Halidemercuri anisoles.[43]

These are prepared in the usual way from the R_2Hg compound and mercuric halides. *Chloride* crystallizes in colorless pearly leaflets. It is soluble in hot benzene, more soluble in chloroform, difficultly soluble in alcohol. M.P. 239° (Cl). It can also be prepared by boiling the $HgCl_2$ double salt of antimony tri-anisyl with alcohol.[44] When it is

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[40] Dimroth, *Ber.* 35 (1902), 2867.

[41] Michaelis and Rabinerson, *Ber.* 23 (1890), 2345. Michaelis, *Ber.* 27 (1894), 257.

[42] *Ibid.* 259.

[43] Michaelis and Rabinerson, *Ber.* 23 (1890), 2344.

[44] Löloff, *Ber.* 30 (1897), 2836.

heated with arsenic trichloride in a water bath it forms anisyl dichlorarsine in good yield.[45] Another preparation is by adding sodium chloride to the "addition" compound of anisole and mercuric hydroxide obtained from anisole and aqueous mercuric acetate at 50°.[46] *Bromide.* Similar to the chloride. M.P. 187° (Br). *Iodide,* colorless pearly leaflets. M.P. 227° (I). The iodide is also obtained by treating an alkaline alcoholic solution of p-hydroxymercuriphenol with methyl iodide.[47]

Long boiling with potassium iodide gives a small amount of inorganic mercury. The solution remains neutral indicating that there has been no splitting of the C—Hg linkage and that R_2Hg has been formed. None of this substance can be isolated. The only organic product is unchanged iodide.[48] This failure to obtain the R_2Hg compound in the para series when it can be obtained in the ortho series corresponds to the results obtained with the acetylated ortho and para hydroxyphenylmercuric chlorides.[49] Apparently potassium iodide causes the "coupling" or "bridging" reaction best when the mercury is ortho to the hydroxyl group. This regularity probably holds true of aromatic amines. o-Acetoxymercuri-p-bromodimethylaniline is readily changed to the R_2Hg compound by potassium iodide.[50] On the other hand p-acetoxymercuri-dimethylaniline is only changed to the iodide by long boiling with potassium iodide.[51]

The corresponding *cyanide* and *sulfocyanate* are prepared in the same way as the halides.[52] Cyanide M.P. 167.5°. Sulfocyanate M.P. 208°.

p-Anisylmercuric oxide, $(CH_3O-C_6H_4-Hg)_2O$.[53]

Prepared from a solution of one of the halides in hot sodium carbonate solution. Recrystallized from alcohol. M.P. 177°. It is very difficultly soluble in water, easily soluble in alcohol and in hot sodium carbonate solution. The solution in water is alkaline but does not absorb carbon dioxide from the air. (CH).

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[45] Roeder and Blasi, *Ber.* 47 (1914), 2752.
[46] Manchot, *Ann.* 421 (1920), 343.
[47] Dimroth, *Ber.* 31 (1898), 2155. *Chem. Zentr.* 1901 I 452.
[48] Unpublished results, Whitmore and Middleton.
[49] Whitmore and Middleton, *J. Am. Chem. Soc.* 43 (1921), 623.
[50] Whitmore, *J. Am. Chem. Soc.* 41 (1919), 1850.
[51] Unpublished results, Whitmore and L. F. Howe.
[52] Michaelis, *Ber.* 27 (1894), 260.
[53] Michaelis and Rabinerson, *Ber.* 23 (1890), 2345.

Derivatives of Phenetole.[54]

o-Mercury Diphenetyl.

1. Prepared from the bromide and sodium amalgam in the usual way.

2. Obtained as a by-product in the treatment of an alkaline solution of o-chloromercuriphenol with ethyl iodide. The o-iodomercuriphenetole first formed probably reacts with the inorganic iodide present forming the R_2Hg compound. It forms shining needles, easily soluble in hot benzene, xylene, alcohol, and chloroform. M.P. 83° (not 224°). It reacts with mercuric salts and with organic and inorganic acids giving the usual products.

3. o-Phenetylmercuric iodide when refluxed with an excess of potassium iodide in dilute alcohol gives a practically quantitative yield of o-mercury diphenetyl.[55]

4. Potassium sulfocyanate gives the same reaction as potassium iodide but the yield of the mercury diphenetyl is not as good.[55]

5. o-Phenetylmercuric iodide dissolves readily in concentrated sodium thiosulfate solution. On standing o-mercury diphenetyl separates.[55]

o-Acetoxymercuri phenetole.

Prepared from the R_2Hg compound and acetic acid in the usual way. Fine white tablets. M.P. 150.5° (CH).

o-Halidemercuri phenetoles.

Prepared in the usual way from the mercury diphenetyl compound and mercuric halides. They are much more soluble in alcohol than the corresponding para compounds. *Chloride.* Shining needles, easily soluble in benzene and chloroform. M.P. 132° (Cl). *Bromide.* If dissolved in alcohol and diluted with water, it gives fine white needles. Recrystallized from benzene or chloroform, it forms four sided shining prisms. M.P. 121° (Br). *Iodide.* Crystallizes from alcohol in thick prismatic needles, from benzene in triangular prisms. M.P. 111.5°. It can also be obtained by treating an alkaline solution of o-chloromercuriphenol with ethyl iodide. It is obtained by adding water to the alcoholic mother liquors from the R_2Hg compound which is formed at the same time.

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[54] Dimroth, *Ber.* 32 (1899), 758. Michaelis, *Ber.* 27 (1894), 261.

[55] Unpublished results, Whitmore and Middleton.

p-Mercury Diphenetyl.[56]

Prepared in the usual way from the bromide and sodium amalgam. It crystallizes from a concentrated solution in benzene in shining leaflets. M.P. 135°. Sp.g. at 15° is 1.0028. Rather difficultly soluble in hot alcohol. (CHHg). Hot concentrated hydrochloric acid readily gives mercuric chloride and phenetole. It reacts with phosphorus trichloride to form mercuric chloride and $C_2H_5O - C_6H_4 - PCl_2$.

The p-mercury diphenetyl cannot be prepared from p-phenetylmercuric iodide and potassium iodide or potassium sulfocyanate as can the ortho compound. The reaction probably takes place to a slight extent as a small amount of inorganic mercury is formed but none of the "coupled" compound can be isolated. The formation of inorganic mercury is not due to a breaking of the C — Hg linkage as no alkali is formed.[57]

Reaction of Phenetole with Mercuric Acetate.

1. In water.[58] *Addition compound of phenetole and mercuric hydroxide.* The reaction is like that of anisole. The white precipitate is filtered after ten days. Recrystallized from dilute alcohol it forms fine needles melting at 135.5°. It gives no mercury reactions with the common reagents. It can be recrystallized from methyl alcohol or water. The water solution reacts with potassium hydroxide giving a precipitate which is soluble in an excess of base. Warmed with dilute HCl it gives phenetole. (CHHg). Treated with ten per cent potassium bromide solution it gives a product melting at 193° from which can be extracted p-bromomercuriphenetole of M.P. 238° (Lit. 241.5°).

2. Without solvent. The acetoxymercuri group is introduced into the para position.[59]

p-Acetoxymercuri phenetole.

Mercuric acetate heated with an excess of phenetole gives crystals which can be recrystallized from dilute acetic acid in tablets. No ortho compound is obtained. M.P. 162° (CHHg). The acetate can also be prepared from p-mercury diphenetyl and glacial acetic acid.[60]

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[56] Michaelis, *Ber.* 27 (1894), 258. *Ann.* 293 (1896), 257.
[57] Unpublished results, Whitmore and Middleton.
[58] Manchot, *Ann.* 421 (1920), 334 ff.
[59] Dimroth, *Chem. Zentr.* 1901 I 453. *Ber.* 35 (1902), 2867.
[60] Michaelis, *Ber.* 27 (1894), 259.

Colorless rhombic tablets. Recrystallized from alcohol it forms long clustered needles. (CH).

p-Propionoxymercuri phenetole.[61]

Prepared by dissolving the R_2Hg compound in concentrated propionic acid and pouring the solution into dilute sodium carbonate solution. White powder. It crystallizes from hot water in fine white silky needles. M.P. 116°. It is difficultly soluble in cold water, easily soluble hot, soluble in alcohol and benzene. (CH). The corresponding *butyrate* is made in a similar way. Fine white needles. M.P. 129° (CH).

p-Halidemercuri phenetoles.[62]

Prepared in the usual way from mercury diphenetyl and mercuric salts in alcohol. *Chloride.* Colorless fine needles, rather difficultly soluble in alcohol, easily soluble in hot benzene and chloroform. M.P. 234° (Cl). The chloride is also obtained by boiling an alcoholic solution of the double compound of mercuric chloride and antimony triphenetyl.[63] *Bromide.* Crystallizes from benzene in fine needles, from chloroform in shining leaflets. Difficultly soluble in alcohol. M.P. 241.5° (Br). The bromide is obtained in an impure form by adding potassium bromide to the addition compound of phenetole and mercuric hydroxide obtained from phenetole and mercuric acetate in water solution.[64] *Iodide.* Small white needles. M.P. 216° (I).

The iodide can also be prepared by treating p-hydroxyphenylmercuric chloride with sodium hydroxide and ethyl iodide.[65]

The *cyanide* and *sulfocyanate* have been made in the same way as the halides. The preparation of the cyanide from mercury diphenetyl and mercuric cyanide in alcohol requires heating at 120° in a sealed tube. It forms fine large pearly leaflets from alcohol. M.P. 158-9°. It is readily soluble in alcohol, less so in benzene and chloroform. (N). The sulfocyanate is prepared in the same way as the cyanide. It is crystallized from alcohol. M.P. 210°. Difficultly soluble in alcohol and benzene.

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[61] Michaelis, *Ber.* 27 (1894), 259.
[62] *Ibid.*
[63] Löloff, *Ber.* 30 (1897), 2842.
[64] Manchot, *Ann.* 421 (1920), 345.
[65] Unpublished results, Whitmore and Middleton.
[66] Michaelis, *Ber.* 27 (1894), 259.

Oxide of p-mercury phenetyl, $(C_2H_5O — C_6H_4 — Hg)_2O$.[66]

It is prepared by dissolving one of the halides in hot sodium carbonate solution and cooling. The white powder is recrystallized from alcohol in fine white needles. M.P. 202°. It is easily soluble in hot alcohol, and hot sodium carbonate solution but difficultly soluble in water. (CH).

Mercury Derivatives of Phenoxyacetic Acid.

p(?)-Hydroxymercuriphenoxyacetic acid.[67]

The anhydride of this acid is obtained by heating phenoxyacetic acid with mercuric oxide until the mixture is soluble in sodium hydroxide. The product consists of white crystals insoluble in water and common solvents, soluble in alkalies. It is decomposed by heat. Concentrated HCl gives mercuric chloride. The sodium salt forms a double compound with alanine which is soluble in water giving a neutral stable solution, but is insoluble in alcohol, ether and benzene.

Similar mercury derivatives have been made from many substituted phenoxyacetic acids.[68] Among these are the o-chlorophenol, thymol, guaiacol, carvacrol, naphthols, salicylic acid, catechol, p-cresol, p-xylenol derivatives of acetic acid, in general, $R — O — CH_2CO_2H$. The sodium salts of the mercury compounds, obtained from these aryloxyacetic acids, form stable water soluble compounds with alanine and with sodium diethylbarbiturate. The mercury compounds themselves are practically insoluble in all solvents and decompose on heating.

Mercury Derivatives of Substituted Phenols.

Derivatives of Halogen Phenols.

p-Hydroxymercuri-o-chlorophenol.[69]

It is prepared by heating o-chlorophenol with mercuric oxide or mercuric salts. Insoluble in water and common solvents, it is soluble in alkalies and acids giving salts. It decomposes on heating and acts with concentrated HCl giving mercuric chloride.

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[67] D. R. P. 261,229. *Chem. Zentr.* 1913 II 193. Fränkel, 671. D. R. P. 264,267. *Chem. Zentr.* 1913 II 1183. *Chem. Abst.* 7 (1913) 4046.

[68] D. R. P. 261,229 loc. cit. D. R. P. 261,875. Fränkel, 670. D. R. P. 264,267 loc. cit.

[69] D. R. P. 234,851. *Chem. Zentr.* 1911 1 1769. *Chem. Abst.* 8 (1914), 1337. Fränkel, 659.

o-Hydroxymercuri-p-chlorophenol.[70] Preparation and properties like those of the o-chlor compound. A similar p-bromo compound has been prepared.

o-Acetoxymercuri-p-bromophenol is obtained as a pink solid by treating p-bromophenol with mercuric acetate in warm water.[70a] It does not dissolve completely in dilute alkali.

Mercury compound of tribromophenol.[71]

The sodium compound of tribromophenol reacts with mercuric acetate giving a yellow crystalline precipitate. This is probably not a true organic mercury compound as it reacts with sodium hydroxide forming HgO. Heated to 110° it gives mercurous bromide and a gray insoluble mercury compound which is perhaps related to dibromophenol. The original mercury compound is probably an O — Hg compound, stable in this case because the o- and p-positions are occupied.

Mercury Derivatives of Nitrophenols.

Nitrophenols having a free ortho or para position react readily with mercuric oxide or mercuric salts either with or without solvents. In the case of picric acid the reaction is very slow as only the positions meta to the hydroxyl are open. Four types of compounds are obtained. The primary product is usually the anhydride of the — HgOH group and the aci-nitro group. As would be expected from this quinoid structure these compounds are highly colored. If the anhydride is treated with sodium hydroxide, a colored sodium salt is obtained. The intense color indicates that it is a salt of the aci-nitro quinoid form rather than a sodium compound of the phenol. If the anhydride or the sodium salt is treated with hydrochloric acid a colorless chloromercuri compound is obtained. If the acidification is done with sulfuric acid, the salt which would be expected is apparently completely hydrolyzed as a colorless hydroxymercuri compound is obtained.

Anhydride of 4-hydroxymercuri-2-acinitro phenol.[72]

The sodium compound of o-nitrophenol in alcohol is shaken with

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[70] Hantzsch and Auld, *Ber.* 39 (1906), 1117. D. R. P. 234,851. *Chem. Zentr.* 1911 I 1769. Fränkel, 660.

[70a] Private communication, G. W. Raiziss.

[71] *Therap. Monatsh.* 51 (1890), 128. Hantzsch and Auld, *Ber.* 39 (1906), 1117. Merck, 1907, p. 282. Torrey and Hunter, *J. Am. Chem. Soc.* 33 (1911), 203.

[72] Hantzsch and Auld, *Ber.* 39 (1906), 1115. D. R. P. 234,851. *Chem. Zentr.* 1911 I 1769. Fränkel, 660. Schamberg, *Chem. Abst.* 11 (1917), 2247.

the calculated amount of mercuric acetate in water. A yellow precipitate hard to filter is obtained. It is insoluble in all solvents. (CH). Ammonium sulfide gives no action. Hydrochloric acid gives the chloromercuric compound and then mercuric chloride. Iodine and bromine give the iodide and bromide of o-nitrophenol of M.P.'s 89° and 88° respectively.

4-Hydroxymercuri-2-nitrophenol.

The solution of the anhydride in sodium hydroxide is treated with dilute sulfuric acid. Pale yellow needles. M.P. 240-50°. It is easily soluble in acetone, giving a slightly yellow solution, less soluble in alcohol, and insoluble in water. (Hg).

Sodium salt of 4-hydroxymercuri-2-acinitrophenol.

It is prepared from the anhydride or the chloromercuri compound and fairly concentrated sodium hydroxide. Recrystallized from dilute alcohol it forms deep red crystals.[73]

4-Acetoxymercuri-2-nitrophenol is obtained as an amorphous solid by heating together water solution of o-nitrophenol and mercuric acetate.[73a]

4-Chloromercuri-2-nitrophenol is prepared from the anhydride and dilute hydrochloric acid. It is recrystallized from absolute alcohol or acetone, forming pale yellow crystals which are soluble in ethyl acetate, slightly soluble in alcohol and ether and insoluble in chloroform. (Hg). The solution in ethyl acetate and acetone is colorless while the solution in pyridine is yellow.

4, 4'-Mercuribis-2-nitrophenol.[74]

The chloride or anhydride is reduced with the calculated amount of a neutral or alkaline reducing agent. Another preparation is by heating an alkaline solution of m-nitro-p-hydroxy phenyl arsenious oxide with mercuric chloride. It is recrystallized from acetone or from pyridine and alcohol. It does not melt at 270°. It is soluble in bases.

Anhydride of 2-hydroxymercuri-4-acinitrophenol.

The preparation from the sodium compound of p-nitrophenol and mercuric oxide is too slow. Mercuric acetate is used. Warming finally

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[73] Schamberg, loc. cit.

[73a] Private communication, G. W. Raiziss.

[74] Launoy and Levaditi, *Compt. rend. soc. biol.* 74 (1913), 18. Cf. Fourneau and Vila, *J. pharm. chim.* (7) 6 (1912), 433. D. R. P. 272,289. *Chem. Zentr.* 1914 I 1469, Fränkel, 661.

gives a yellow powder which is slightly soluble in water, soluble in pyridine, but insoluble in other solvents. (NHg). It does not react with potassium iodide or hydrogen sulfide. Concentrated acids give mercuric salts. It forms a scarlet compound with one molecule of pyridine. It loses this pyridine at 190°, giving the original yellow compound. When the anhydride is treated with iodine it gives the iodonitrophenol of M.P. 152°.

Sodium salt of 2-hydroxymercuri-4-acinitrophenol.

It is prepared from the anhydride and sodium hydroxide in the form of yellow crystals containing one-half molecule of water of crystallization. It darkens on heating giving a slight explosion. (H_2O,Na).

2-Hydroxymercuri-4-nitrophenol.

It is prepared from the sodium salt and a slight excess of dilute sulfuric acid or from a solution of the sodium salt treated with carbon dioxide. It forms an amorphous powder. M.P. 206°. It is soluble in acetone, alcohol, and ethyl acetate giving entirely colorless solutions. Even a pyridine solution is only slightly yellow. (Hg).

2-Acetoxymercuri-4-nitrophenol is obtained as a yellow amorphous solid by warming p-nitrophenol with mercuric acetate in water solution.[74a] The product is crystallized three times from glacial acetic acid. (HgN). It is easily soluble in dilute alkali.

2-Chloromercuri-4-nitrophenol.

Prepared from the anhydride and hydrochloric acid. It is recrystallized from alcohol. M.P. 175°. Almost colorless. It is soluble in ethyl acetate and alcohol giving colorless solutions. (Hg).

Anhydride of 2-hydroxymercuri-4-acinitro-6-nitrophenol.[75]

It is made from freshly prepared mercuric oxide and the calculated amount of dinitrophenol boiled for 16 hours. The citron yellow powder is very little soluble in water and alcohol, insoluble in other solvents except pyridine with which it forms a compound. The water solution is not precipitated by ammonium sulfide, potassium iodide or alkali, and is practically a non-conductor. The pyridine compound is precipitated from a pyridine solution by adding ether. It is a dark yellow solid, insoluble in common solvents. (CH, pyridine). It loses

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[74a] Private communication, G. W. Raiziss.

[75] Hantzsch and Auld, *Ber.* 39 (1906), 1105.

pyridine on heating. The anhydride reacts with bromine in potassium bromide solution forming the bromodinitrophenol of M.P. 117°.

Sodium salt of 2-hydroxymercuri-4-acinitro-6-nitrophenol.

The chloride is treated with fairly concentrated sodium hydroxide. It crystallizes from dilute alcohol in fine orange prisms. It explodes on vigorous heating. The crystals contain one molecule of water. (Na, H_2O). Dilute HCl forms the chloromercuri compound and dilute sulfuric acid forms the hydroxymercuri compound.

2-Hydroxymercuri-4, 6-dinitrophenol.

The corresponding sodium compound is treated with dilute sulfuric acid. The product crystallizes from absolute alcohol as a colorless microcrystalline powder. It is slightly soluble in alcohol and ethyl acetate giving colorless solutions. It is easily soluble in pyridine with a yellow color. (Hg).

2-Chloromercuri-4, 6-dinitrophenol.

It is prepared from the anhydride and dilute hydrochloric acid. The colorless product is recrystallized from alcohol by adding water. M.P. 182° decomp. It gives almost colorless solutions in alcohol and chloroform, entirely colorless in acetic acid and ethyl acetate. (ClHg). *A benzoyl derivative* is obtained by the Schotten-Baumann reaction.

Mercury derivatives of picric acid.[76]

The compounds most easily obtained are undoubtedly O — Hg compounds.

Anhydride of 3-hydroxymercuri-4-acinitro-2, 6-dinitrophenol.

When the mercury picrate obtained from picric acid and mercuric oxide is boiled with water for a few days the solution becomes indifferent to hydrogen sulfide. The best method of preparation is to boil the solution for only a few hours and then cool it. The C — Hg compound separates first. Washing with alcohol removes any O — Hg compound mixed with it. It forms small yellow crystals which decompose on heating. The yellow water solution of the substance is neutral and gives no precipitate with sodium hydroxide, potassium iodide, ammonium sulfide, and is practically a non-conductor. It is only slightly

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[76] *Ibid.* 1110.

soluble in common solvents. (HgN). Dilute hydrochloric acid gives the corresponding chloromercuri compound.

Hydroxymercuri-picric acid.

The sodium salt or the anhydride is treated with dilute sulfuric acid. The product is yellow at first but gradually becomes colorless. The solution in alcohol or acetone is colorless. It is almost insoluble in water even on boiling. It apparently has no aci- form.

Sodium salt of 3-hydroxymercuri-4-acinitro-2, 6-dinitrophenol.

It is prepared from the chloromercuri compound and sodium hydroxide. It decomposes on rapid heating. (Na). It crystallizes from alcohol in beautiful yellow needles which are easily soluble in water.

Chloromercuri-picric acid.

The anhydride is treated with dilute hydrochloric acid. It crystallizes from chloroform in pale yellow crystals. M.P. 118°. It is easily soluble in alcohol and pyridine giving a deep yellow color, difficultly soluble in chloroform but with a much brighter color. (Hg).

Mercury Derivatives of Amino Phenols.

p-Chloromercuri-o-aminophenol.[77]

This is the probable structure of the product obtained by adding sodium hydroxide and mercuric chloride to the hydrochloride of m-amino-p-hydroxyphenyl dichlorarsine and precipitating the resulting solution with acetic acid.

4, 4′-Mercuribis-2-aminophenol.[78]

Prepared by vigorous reduction of the chloromercuri or hydroxymercuri compound of o-nitrophenol in neutral or alkaline solution. The *diacetyl derivative* of this substance has been made.[79]

Several mercury derivatives of m-dimethylaminophenol have been prepared.[80] *Acetoxymercuri-m-dimethylaminophenol* and its *acetyl derivative* have been made and tested with sulfides. The former is reactive and the latter unreactive. A remarkable property of this type of mercury compound is that the mercury diphenyl derivative can be prepared directly from mercuric acetate and the quarternary ammonium acetate obtained from the amino phenol. This reaction is

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[77] D. R. P. 272,289. *Chem. Zentr.* 1914 I 1469.

[78] Launoy and Levaditi, loc. cit. Fourneau and Vila, loc. cit.

[79] *Chem. Abst.* 7 (1913), 1384.

[80] Kharasch and Chalkley, private communication.

without parallel in the chemistry of organic mercury compounds. It may be represented by the equation,

$$Hg(OAc)_2 + 2HO - C_6H_4 - N(CH_3)_3OAc \rightarrow$$
$$2HOAc + [HO - C_6H_3 - N(CH_3)_3OAc]_2Hg.$$

p-Oxyphenylethyl amine reacts with sodium hydroxide and mercuric chloride giving a white precipitate, $C_9H_{10}ONHg$.[81]

4-Acetoxymercuri-3-acetaminophenol is obtained as a white powder by warming o-acetaminophenol and mercuric acetate in water solution.[81a] It is soluble in dilute alkali.

2-Acetoxymercuri-4-chloro-6-aminophenol is obtained as a yellow powder by warming p-chloro-o-aminophenol with mercuric acetate in methyl alcohol solution.[81a] It is soluble in dilute alkali.

Aminophenol sulfonic acid III forms a compound on heating with mercuric oxide.[82]

p-Chloro-o-nitrophenol forms a compound when heated with mercuric oxide.[83]

When the chloronitrophenol is treated with mercuric acetate in water or in methyl alcohol no organic mercury compound is obtained.[83a] *2-Nitro-5-iodophenol* reacts with mercuric acetate in boiling water giving an organic mercury compound.[83a]

6, 6′-Mercuribis-1-hydroxy-2-methyl-benzene-4-arsonic acid.

It is prepared by the neutral or alkaline reduction of the product obtained by heating o-cresol arsonic acid with mercuric oxide.[84]

Mercury Derivatives of p-Cresol.[85]

p-Cresol reacts with alcoholic mercuric acetate even more readily than does phenol. At room temperature the reaction takes two days, at 90° it is complete in thirty minutes. About equal amounts of the mono- and di-mercurated products are formed. The latter separates almost pure. The mother liquor treated with sodium chloride gives

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[81] D. R. P. 279,957. *Chem. Zentr.* 1914 II 1334. Fränkel, 661.

[81a] Private communication, G. W. Raiziss.

[82] D. R. P. 281,009. *Chem. Zentr.* 1915 I 73.

[83] D. R. P. 234,851. *Chem. Zentr.* 1911 I 1769. Fränkel, 660.

[83a] Private communication, G. W. Raiziss.

[84] D. R. P. 255,030. *Chem. Zentr.* 1913 I 353.

[85] Dimroth, *Chem. Zentr.* 1901 I 450. *Ber.* 35 (1902), 2856. J. Rother, *Dissert.* Berlin, 1911, p. 9.

chloromercuri-p-cresol. The diacetoxymercuri-p-cresol separates almost pure.

o-Acetoxymercuri-p-cresol.

The anhydride of hydroxymercuri-p-cresol is heated with dilute acetic acid. Cooling gives colorless leaflets. Put in a bath at 150° it melts at 163° (CHHg). When the acetate is treated with potassium iodide no iodomercuri compound is obtained but the product is "decomposed." Perhaps the C — Hg linkage is broken as in the case of the mercurated naphthols and phenols.[86]

A sodium hydroxide solution of the acetate reacts with benzene diazonium chloride giving a red precipitate of *o-benzeneazo-o′-acetoxymercuri-p-cresol* which crystallizes from acetic acid in red needles. It darkens at 262° and melts with decomposition at 269° (CHHgN). It is difficultly soluble in all solvents. Concentrated hydrochloric acid replaces the mercury by hydrogen.

Anhydride of o-hydroxymercuri-p-cresol.

The chloride dissolves in sodium hydroxide giving a clear solution from which carbon dioxide precipitates the anhydride. Another method of preparation is the treatment of an alcoholic solution of the chloride with the calculated amount of boiling sodium carbonate. The product is a fine white powder, insoluble in water and common solvents. It dissolves in hot phenol but gives poor crystals. (CHHg).

Sodium compound of o-hydroxymercuri-p-cresol.

The anhydride is dissolved in a very slight excess of warm 12% sodium hydroxide free from carbonate; cooling the solution gives needle crystals which turn yellow in light. (Na).

Chloromercuri-p-cresol.

The warm mother liquor from the diacetoxymercuri compound obtained from mercuric acetate and p-cresol is treated with sodium chloride. Fine needles separate. These are extracted with cold alcohol which dissolves the mono compound and leaves the di-. The alcoholic extract is concentrated and treated with water. The substance is recrystallized from hot benzene. (CHHg). It is easily soluble in cold alcohol, very little in cold benzene, fairly soluble in boiling water. It melts at 166° forming a clear liquid which becomes cloudy at 176°

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[86] Brieger and Schulemann, *J. prakt. Chem.* (2) 89 (1914), 104.

and solidifies at 183°. A *benzoyl derivative* can be prepared by the Schotten-Baumann reaction. It crystallizes from benzene in very fine needles. Put in a bath at 220° it melts at 241-2° (CHHg). The chloromercuricresol reacts with benzene diazonium chloride giving *o-benzeneazo-o′-chloromercuri-p-cresol.* This is difficultly soluble in alkali. It gives no acid addition products like those obtained from the corresponding phenol compounds.

o-Iodomercuri-p-cresol.

It cannot be made from the chloride mother liquors containing acetic acid as mercuric iodide splits out on addition of potassium iodide. The pure chloride is treated with boiling water and the calculated amount of potassium iodide. On cooling fine needles are formed. (CHHgI). It turns yellow at 145° and red at 170° but does not melt. Part of it sublimes. It is easily soluble in ether and alcohol, difficultly in benzene and chloroform, hardly soluble in ligroin. It is stable to boiling water but is gradually decomposed by long boiling in alcohol or benzene. The iodide dissolved in ether and shaken with a slight excess of iodine in potassium iodide solution decolorizes the latter. The ether layer is shaken with more potassium iodide solution to remove all of the mercuric iodide formed. The ether layer contains o-iodo-p-cresol.

Diacetoxymercuri-p-cresol.[87]

This substance crystallizes from the reaction mixture of p-cresol and mercuric acetate. The product is recrystallized from dilute acetic acid and air dried. It contains one molecule of water of crystallization. This cannot be removed without driving off acetic acid also. It decomposes at 200°. The product obtained by heating to drive off the water of crystallization is probably *o-hydroxymercuri-o′-acetoxymercuri-p-cresol* or its inner anhydride.

Derivatives of p-Cresol Methyl Ether.[88]

p-Cresol methyl ether reacts with aqueous mercuric acetate giving a crystalline product which gives analyses for carbon, hydrogen and mercury which agree with the formula

$$3CH_3-C_6H_4OCH_3.Hg(OAc)_2.2HgO.$$

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[87] **Brit. Pat. 24,981. *Chem. Abst.* 6 (1912), 1547.**

[88] **Manchot, *Ann.* 421 (1920), 337.**

The substance is obtained by three different methods of preparation. It is recrystallized from 20% acetic acid or from dilute alcohol. Ammonium sulfide and sodium hydroxide give no mercuric reactions. M.P. 132°.

o-Chloromercuri-p-cresol methyl ether.

This substance is obtained by dissolving the above product in dilute alcohol and adding hot 10% sodium chloride solution. The white voluminous precipitate crystallizes from alcohol in white needles. M.P. 162° (CHHgCl). It gives no mercury reactions with sodium hydroxide, ammonium hydroxide or ammonium sulfide.

p-Xylenol reacts with a methyl alcohol solution of mercuric acetate giving an acetoxymercuri compound.[89]

Derivatives of Thymol.[90]

One or two mercury atoms can be introduced into thymol depending on the amount of mercuric acetate used.

p(?)-Chloromercuri thymol.

Equal molecules of thymol and mercuric acetate are boiled with alcohol containing a little acetic acid. On cooling a very small amount of the di-mercurated product crystallizes out. The filtrate is treated with sodium chloride solution which precipitates a mixture of the mono- and di-compounds. The pure mono compound is obtained after several crystallizations from 40% alcohol. It forms fine needles. M.P. 139.5° (CHHg). It is easily soluble in dilute sodium hydroxide.

Diacetoxymercuri thymol.

Thymol is boiled with two molecules of mercuric acetate in alcohol containing a trace of acetic acid. The crystals which separate are recrystallized from a mixture of ethyl acetate and acetic acid. (CHHg). Placed in a bath at 190° it melts at 215-6°. The sodium salt crystallizes in plates from a warm solution in fairly concentrated sodium hydroxide.

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[89] D. R. P. 250,746. *Chem. Zentr.* 1912 II 1245. Fränkel, 660. *Chem. Abst.* 7 (1913), 3819.

[90] *Therap. Monatsh.* 51 (1890), 128. Dimroth, *Ber.* 35 (1902), 2864. Merck, 1907, p. 281.

Derivatives of Phenol Sulfonic Acids.[91]

Mercury-p-phenol sulfonate in a carbonate solution does not attack metal instruments. The compound of the sulfonate with ammonium tartrate is known as "Asterol."[92]

An alkaline solution of phenol disulfonic acid reacts with mercuric oxide giving a C — Hg compound which is soluble and does not precipitate albumen.[93]

Aminophenol sulfonic acid gives C — Hg compounds.[94] Mercury sozoiodol is not an organic mercury compound but a mercurous salt of di-iodo-p-phenol sulfonic acid.[95]

Mercury Derivatives of Naphthols.

The alkali compounds of the naphthols react with mercuric solutions giving compounds which appear to be O — Hg compounds. These often change on standing from red or yellow to white. This color change may indicate a change to a C — Hg compound.[96]

$\beta - C_{10}H_7OHgCl$(?) is obtained in this way. (CHClHg). It is soluble in alcohol especially on heating, very little soluble in water. Alcohol solution gives colorless prisms which gradually darken. This substance may be a C — Hg compound.

$\beta(C_{10}H_7 - O)_2Hg$.(?). The first precipitate formed is yellow but soon turns white. It is insoluble in common solvents but dissolves in phenol or alcoholic phenol. (CHHg).

$\beta - C_{10}H_7 - OHgOAc$(?). The above compound is treated with acetic acid. (CHHg). The product forms colorless crystals, soluble in alcohol, very little soluble in water.[97]

4-Acetoxymercuri-α-naphthol.

It is prepared from the naphthol and mercuric acetate in acetic acid solution. The product is precipitated by the addition of water.[98] If the reaction is carried out in dilute acetic acid white crystals

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[91] D. R. P. 104,904 and 121,656. Fränkel, 674.

[92] D. R. P. 157,663. Fränkel, 674.

[93] Lumière, *Compt. rend.* 132 (1901), 145. *Chem. Zentr.* 1901 I 455.

[94] D. R. P. 281,009. Fränkel, 670.

[95] *Chem. Zentr.* 1912 I 1521.

[96] Desesquelle, *Bull. soc. chim.* (3) 11 (1894), 264.

[97] Merck, 1907, p. 279. *Realenzyk. Pharm.* VI 491. Brit. Pat. 24,981. *Chem. Abst.* 6 (1912), 1547.

[98] Bamberger, *Ber.* 31 (1898), 2626.

separate which turn intensely yellow on filtering and washing. Ammonium sulfide does not react at once. The yellow product contains no acetate. The analyses for carbon, hydrogen and mercury agree with the assumption that the compound is a hydroxymercuri naphthol. It is assumed to be such a compound having the mercury in the β position. It is also suggested that the color may be due to a quinoid structure. In this case a molecule of water of crystallization would have to be assumed. The C — Hg linkage is split by alkali chlorides, bromides and iodides with increasing ease forming free alkali.

2, 4 Diacetoxymercuri-α-naphthol.[99]

It is prepared from the naphthol and the two molecules of mercuric acetate in 30% acetic acid. It forms colorless needles which are recrystallized from acetic acid. (Hg,HOAc). It is stable to ammonium sulfide but reacts with alkali halides the same as the mono compound.

1-Acetoxymercuri-β-naphthol.[100]

Acetic acid solutions of the naphthol and mercuric acetate are mixed in the cold. The crystalline precipitate is soluble in dilute sodium hydroxide and is precipitated by acetic acid. (CHHg). It forms white shining needles, if rapidly heated it melts at 185°, with blackening and frothing. It is only slightly soluble in hot water, benzene, xylene, ligroin, ether, chloroform, alcohol, and acetone. Soluble in acetic acid and sodium hydroxide. The solution in sodium hydroxide gives a yellow precipitate with ammonium sulfide. This only turns black on heating.

Beta-naphthol reacts with mercuric acetate in cold methyl alcohol giving a product which is described as "5-acetoxymercuri-β-naphthol."[100a] It is soluble in 200 parts of ethyl acetate and in 50 parts of a mixture of 3 parts of toluene and 1 part of 95 per cent ethyl alcohol.

β-Naphthol carboxylic acid.

Anhydride of 1-hydroxymercuri-4-carboxyl-β-naphthol.[101]

Prepared from the naphthol carboxylic acid and mercuric acetate. The solution in dilute sodium hydroxide reacts with diazosulfanilic

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[99] Brieger and Schulemann, *J. prakt. Chem.* (2) 89 (1914), 134.

[100] Bamberger, loc. cit. 2624. Brieger and Schulemann, loc. cit. 132. Dimroth, *Ber.* 32 (1899), 765.

[100a] Private communication, G. W. Raiziss.

[101] Brieger and Schulemann, *J. prakt. Chem.* (2) 89 (1914), 180.

acid and urea forming the compound *1-azobenzene sulfonic acid-4-carboxyl-β-naphthol.* This reaction proves the position of the mercury in the original substance. A remarkable fact about this replacement of mercury is that it takes place more rapidly than does the coupling of the diazosulfonic acid with the unmercurated naphthol carboxylic acids. The anhydride when treated with iodine in potassium iodide and acidified with acetic acid gives a mixture from which can be extracted *1*-iodo-*4*-carboxyl-β-naphthol and beta naphthol-*4*-carboxylic acid. The formation of the latter is probably due to the action of hydriodic acid liberated by the action of the acetic acid on the iodide solution.

Naphthol sulfonic acids.[102]

2-Acetoxymercuri-1-naphthol-4-sulfonic acid sodium salt.

It is prepared from the impure sodium salt and mercuric acetate in water. It gives a yellow brown substance. Recrystallization from dilute acetic acid gives a yellow brown substance. (HgNa). Sodium hydroxide and ammonium sulfide give no reaction. Halogen salts split the C — Hg linkage. No di-mercurated product could be made from this acid.

1-Acetoxymercuri-2-naphthol-6-sulfonic acid sodium salt.

It is prepared by mercuration in water solution. White crystals, difficultly soluble except in presence of a little sodium hydroxide or acetic acid. (HgNa). Very stable to ammonium sulfide, except in the presence of halide salts which exert a "loosening" effect on the C — Hg linkage. Diazo solutions couple with the compound by replacing the mercury group. After the reaction the mercury can be precipitated by ammonium sulfide. No di-mercury compound has been obtained.[103]

1-Naphthol-5-sulfonic acid treated with mercuric acetate gives only tarry substances and considerable mercurous acetate.

1, 8-Amino naphthol-4, 6-disulfonic acid salts and their benzoyl and dibenzoyl derivatives react with mercuric acetate giving colored mercuric compounds. No definite C — Hg compounds have been isolated. They are apparently very unstable.

1, 8-Amino naphthol-4-sulfonic acid gives even less stable mercury compounds.

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[102] Brieger and Schulemann, *ibid.* 138 ff.

[103] D. R. P. 143,726. Fränkel, 662.

1-Hydroxymercuri-2-naphthol-3, 6-disulfonic acid.[104]

The corresponding naphthol compound is heated with mercuric oxide. Alkaline or neutral reduction changes it to the corresponding R_2Hg compound.

1, 8-Dihydroxy-3-6-disulfonic acid.

This substance gives yellow mercury compounds which cannot be isolated pure. 1, 8-Amino naphthol-3, 6-disulfonic acid gives very unstable mercury compounds. 2-Naphthol-3, 6-disulfonic acid gives mercury compounds when treated with alkali carbonates and mercuric chloride.[105]

Mercury Compounds of Dihydroxybenzenes.

Pyrocatechol reduces mercuric acetate to the mercurous compound.[106, 107]

3-Mercuri-2-hydroxy-4-methyl anisole compounds have been made.[108]

5-Acetoxymercuri-2-hydroxy-anisole is prepared by warming guaiacol and mercuric acetate in methyl alcohol. It is soluble in dilute alkali.[108a]

Guaiacol acetate reacts with mercuric acetate in warm methyl alcohol giving a *diacetoxymercuri guaiacol acetate* which is soluble in water and in dilute alkalies. (Hg). The position of the mercury atoms has not been determined.[108a]

3-Acetoxymercuri-2-hydroxy-5-nitro-anisole is obtained by warming p-nitroguaiacol with a water solution of mercuric acetate on the water bath for about one hour.[108a] The product is soluble in dilute alkali. (Hg, high).

p-Nitroguaiacol acetate when warmed with mercuric acetate in methyl alcohol gives a mercury compound which is not completely soluble in dilute sodium hydroxide.[180a] The analysis for mercury comes between the values for one and two atoms of mercury.

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[104] D. R. P. 255,030. *Chem. Zentr.* 1913 I 353.

[105] D. R. P. 143,448. Fränkel, 661.

[106] Leys, *J. pharm. chim.* (6) 21 (1905), 388. *Chem. Zentr.* 1905 I 1531.

[107] Brit. Pat. 24,981. *Chem. Abst.* 6 (1912), 1547.

[108] D. R. P. 250,746. *Chem. Zentr.* 1912 II 1245.

[108a] Private communication, G. W. Raiziss.

Derivatives of Resorcinol.[109]

The reaction between resorcinol and mercuric acetate in water solution is complete in 15 minutes. The solution is filtered at once into a concentrated sodium chloride solution.

Chloromercuri-resorcinol.

The chloride mixture obtained from resorcin is extracted with ether which dissolves all but a slight residue. Most of the ether is distilled off and the residue allowed to crystallize. The mono compound is then extracted from the mixture by chloroform. Prisms containing chloroform are obtained. The chloroform compound melts at 105° while the pure compound melts at 123° and turns blood red at 170° (CHClHg). It is easily soluble in ether. It is difficultly soluble in cold water, soluble in warm water but it soon changes to a fine yellow powder which may be the inner anhydride of the o-hydroxymercuri compound. The solution in sodium hydroxide turns yellow and then darker, finally giving a black precipitate. Ammonium sulfide gives HgS at once.

Dichloromercuri-resorcinol.

Obtained from the residue insoluble in chloroform. Dissolved in ether it gives a white powder on evaporation. It darkens about 200° without melting. (Hg). It is difficultly soluble in alcohol. Sodium hydroxide decomposes it even more readily than it does the mono compound giving a black precipitate.

6-Acetoxymercuri-2-nitro-resorcin is prepared from 2-nitro-resorcin and mercuric acetate.[109a] (N). The corresponding *hydroxymercuri* compound is obtained from the nitroresorcin and freshly precipitated mercuric oxide. The *chloromercuri* product is obtained from the hydroxide by dilute hydrochloric acid. (NHg).

Triacetoxymercuri-phloroglucin.[110]

Obtained from phloroglucin and mercuric acetate. Insoluble in water and all common solvents. It is insoluble in solutions of sodium chloride, sodium fluoride, dilute sulfuric acid, dilute nitric acid, ammonium hydroxide and potassium hydroxide, but is soluble in hydrochloric acid and in solutions of potassium cyanide, iodide, bromide,

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[109] Dimroth, *Ber.* 35 (1902), 2865. Leys, *J. pharm. chim.* (6) 21 (1905), 338. *Chem. Zentr.* 1905 I 1531. Merck, 1907, p. 280. *Realenzyk. Pharm.* VI 503.

[109a] Private communication, G. W. Raiziss.

[110] Leys, loc. cit.

sodium thiosulfate, sodium sulfite, and potassium sulfocyanate. This compound is described as an O — Hg compound but it may very likely be a true organic mercury compound. The insolubility in alkali does not necessarily mean the absence of free hydroxyl groups.

Allyl and Propenyl Compounds of Phenol Ethers.[111]

The propenyl compounds react with mercuric acetate giving mercurous acetate and a glycol, R — CHOH — CHOH — CH_3. The allyl compounds give addition compounds containing basic mercuric acetate. These addition compounds usually occur in two isomeric forms, one crystalline and the other amorphous or syrupy. One of these forms may be a polymer of the other. If they are formed by an actual addition to the double bond the isomers may be of the two types R — CH_2 — CHOH — CH_2HgOAc and R — CH_2 — CH(HgOAc) — CH_2OH. Usually mercury adds to the carbon having the most hydrogen atoms.[112] Manchot believes that the mercurated products are simply molecular compounds of the allyl compound and basic mercuric salts.[113] If this theory is correct one of the isomers may be the molecular compound and the other may be the result of a true addition to the double bond. The problem of the structure of these addition compounds is bound up with that of the mercury compounds obtained from ethylene compounds of other kinds. The fact that all of these compounds react with acids giving the original unsaturated compounds throws doubt on their structure as true compounds of the type R — CHOH — CH(HgX) — R. Such a structure would be expected to give a saturated alcohol, R — CHOH — CH_2 — R. In the case of the mercurated allyl compounds treatment with zinc and sodium hydroxide gives the original allyl compounds in the same way as do acids.

The difference in the behaviour of propenyl and allyl compounds to mercuric acetate is recommended as a means of distinguishing and separating these types of compounds.[114] The propenyl compounds give an almost immediate precipitate of mercurous acetate whereas the

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[111] Balbiano and Paolini, *Ber.* 35 (1902), 2994; 36 (1903), 3575. Balbiano, *Ber.* 42 (1909), 1503. Manchot, *Ann.* 421 (1920), 316. Balbiano and Paolini, *Gazz. chim. ital.* 36 I (1906), 244.

[112] Sand and Singer, *Ber.* 35 (1902), 3170.

[113] Manchot, loc. cit. 316.

[114] Balbiano and Paolini, *Ber.* 36 (1903), 3578. Balbiano, *Ber.* 42 (1909), 1503.

allyl compounds give no precipitate, except in the case of apiol, the mercury compound of which is rather insoluble.[115]

The propenyl compounds which have been found to give glycols are anethole, isosafrol, isoeugenol methyl ether, isoapiol, asarone, and isomyristicine.[116]

The allyl compounds which give addition products containing basic mercuric acetate or its constituents are methyl chavicol, safrol, eugenol methyl ether, apiol and myristicin.[117] Of these, apiol gives only one acetate and one chloride instead of the usual pair of isomers. Perhaps this is connected with the fact that apiol has a group in the ortho position to the allyl group.

Methyl chavicol, p-allyl anisole.[118]

Treatment with mercuric acetate gives a thick syrup which is apparently a mixture as it gives two different chlorides and bromides. The acetate is soluble in sodium carbonate and sodium hydroxide. (CHHg). When the solution in sodium hydroxide is treated with zinc it gives methyl chavicol in 50% yield. If the syrupy acetate is dissolved in alcohol and treated with concentrated potassium chloride it gives a yellow resin and a solution.[119] The resin hardens. When powdered it softens at 55° but gives no melting point. The mother liquor on dilution deposits white needle crystals which are almost insoluble in cold water but are soluble in hot water and alcohol. M.P. 81-2°. Both the crystalline and amorphous chlorides react with zinc and sodium hydroxide giving methyl chavicol. When an alcoholic solution of the syrupy acetate is refluxed with potassium chloride a solution results. On cooling, needle crystals of the chloride separate. M.P. 81-2° (CHClHg). The mother liquor gives a resin which hardens and can be powdered. Yellow amorphous. (ClHg). Only a small amount is obtained.[120] The acetate treated with potassium bromide gives a small amount of an amorphous product and a crystalline compound melting at 70-1°, which is soluble in hot water, alcohol and slightly in ether. (CHBrHg).

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[115] Balbiano and Paolini, loc. cit. 3582.

[116] Balbiano, *Gazz. chim. ital.* 36 I (1906), 244.

[117] *Ibid.*

[118] Balbiano and Paolini, *Ber.* 36 (1903), 3580. *Gazz. chim. ital.* 36 I (1906), 264. Balbiano, *Ber.* 42 (1909), 1505.

[119] Balbiano and Paolini, *Ber.* 36 (1903), 3580.

[120] Balbiano, *Gazz. chim. ital.* 36 I (1906), 266.

Safrol, methylene ether of p-allyl pyrocatechol.[121]

The action of mercuric acetate gives a syrupy acetate. (HgCH). If the reaction mixture is allowed to stand for several months, a crystalline form of the acetic separates. (HgCH). This form of the acetate consists of white crystals insoluble in water, ether, soluble in alcohol, especially hot, decomposed by hot water. Distilled with 25% phosphoric acid it gives safrol. The syrupy acetate resembles glucose syrup, it is soluble in alcohol, practically insoluble in ether, soluble in hot water, very little soluble cold. Hydrogen sulfide gives HgS and safrol. The crystalline acetate gives a crystalline *chloride* which decomposes at 170°. The syrupy acetate gives a *chloride* which crystallizes from hot alcohol in hard rosetted prisms which melt at 138° (HgClCH). Both of the isomeric chlorides give safrol when treated with zinc and sodium hydroxide. The chloride which melts at 138° has recently been obtained by Manchot[122] from the reaction mixture of safrol and mercuric acetate in water treated with 10% sodium chloride. He describes the substance as crystallizing from alcohol in long white star-clustered monoclinic needles of M.P. 136-7°. The substance does not give mercury reactions with ammonium sulfide, sodium hydroxide or ammonium hydroxide. Warming with dilute HCl gives an odor of safrol. The chloride is very little soluble in water, very soluble in sodium hydroxide, reprecipitated by dilute HCl. (CHHgCl).

The corresponding *bromide*, $C_{10}H_{10}O_2Hg(OH)Br$, is obtained by treating the safrol reaction mixture with 10% potassium bromide. The crude precipitate melts at 144° and gives no mercury reactions with ammonium sulfide or ammonium hydroxide. It is recrystallized by dissolving in alcohol and diluting with water. It forms long silky flat white needles. M.P. 144-5°. It is difficultly soluble in water and benzene, very soluble in sodium hydroxide, reprecipitated by hydrochloric acid. (CHBrHg). The *iodide* is made in the same way and has entirely similar reactions and properties. M.P. 152.5° (CHHgI). One anomalous property is its reaction with sulfides. It does not react with ammonium sulfide but is blackened by hydrogen sulfide.[123] This difference is perhaps due to some protective action of the basic solution.

The corresponding *hydroxide*, $(C_{10}H_{10}O_2HgOH)OH$, as Manchot formulates it, is obtained from the bromide by moist silver oxide.

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[121] Balbiano and Paolini, *Ber.* 35 (1902), 2998. Balbiano and Paolini, *Ber.* 36 (1903), 3578. Balbiano, *Ber.* 42 (1909), 1505. Manchot, *Ann.* 421 (1920), 320.

[122] Manchot, loc. cit. 320.

[123] *Ibid.* 325.

The aqueous solution obtained is slightly alkaline to litmus but not to phenolphthalein or curcumine. HCl gives a precipitate of the chloride. Heating this mixture gives an odor of safrol. The base treated with potassium bromide gives a precipitate of the *bromide.*

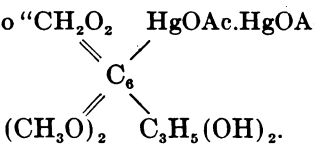
Safrol treated with three molecules of mercuric acetate gives a solution from which a chloride precipitates a substance which Manchot thinks may be $C_{10}H_{10}O_2.HgCl_2.HgO$. (CHHg).

Eugenol methyl ether, dimethyl ether of p-allyl pyrocatechol.[124] (CHHg).

The acetate obtained is a mixture, as it gives two isomeric chlorides. One of these chlorides crystallizes in small transparent prisms, very little soluble in hot water, soluble in alcohol. M.P. 112-113° (CHHgCl). The isomeric chloride is formed as a syrup which gradually hardens. It is amorphous. (ClHg, high). Both the chlorides give methyl eugenol on treatment with zinc and sodium hydroxide. Manchot has obtained the crystalline chloride by treating the reaction mixture containing the acetate with 10% sodium chloride.[125] He obtained silky needle crystals and a brown smeary product. The crystals are soluble in water, while the amorphous product is insoluble. The crystals melt at 112-5° (CHHgCl). Ammonium hydroxide and ammonium sulfide give no reaction. Sodium hydroxide gives a white precipitate, soluble in excess. Hydrochloric acid gives methyl eugenol. A peculiar reaction was noted by Manchot in the action of the chloride with 30 per cent hydrogen peroxide. Mercuric oxide separates at once. Considerable resin is formed at the same time.

Isoapiol, 2, 5-(or 2, 3-)-Dimethyl ether, 3, 4-(or 4, 5-)-methylene ether of 2, 3, 4, 5-tetrahydroxy-1-propenylbenzene.[126]

This propenyl compound not only reduces mercuric acetate to the mercurous compound forming a glycol but acts further with mercuric acetate giving a substance which may be a ring mercurated compound. This compound softens at 160° and melts at 174°. The composition corresponds to



$$\begin{array}{ccc} \text{“}CH_2O_2 & & HgOAc.HgOAc\text{”} \\ & C_6 & \\ (CH_3O)_2 & & C_3H_5(OH)_2. \end{array}$$

[124] Manchot, loc. cit. 326. Balbiano, loc. cit.

[125] Manchot, loc. cit. 326.

[126] Balbiano and Paolini, *Ber.* 36 (1903), 3583.

Apiol, allyl compound corresponding to isoapiol.[127] The reaction with mercuric acetate is more rapid than in the other allyl compounds studied. Crystals start depositing in an hour and the reaction is ended in about five hours. The acetate is recrystallized from alcohol. Only one acetate is obtained. It forms fine needles almost insoluble in water, little soluble in cold alcohol, but soluble hot. (CHHg). M.P. 157-8°. Treatment of the acetate with zinc and sodium hydroxide, followed by steam distillation, gives apiol.[128]

A benzoyl derivative can be prepared. This is an oil boiling at 165°at 4 mm. Saponification and acidification gives hydroxyapiol and benzoic acid. Eugenol treated with three molecules of mercuric acetate gives a product which is not well defined but may be $C_{10}H_{11}O_2.HgCl_2.HgO$.[129]

Mercury Derivatives of Saligenin.[130]

Anhydride of 2-Hydroxy-3, 5-dihydroxymercuribenzyl Alcohol.

Saligenin is refluxed with mercuric acetate in alcohol containing a small amount of acetic acid. On standing over night the solution deposits hard aggregates of needle crystals. The compound is insoluble in water and common solvents. It dissolves in hot glacial acetic acid, in hot acetic anhydride, and in alkalies. It is insoluble in ammonium hydroxide. A water suspension is not changed by hydrogen sulfide. An alkaline solution reacts with hydrogen sulfide giving a black precipitate after several hours. It darkens and gradually decomposes on heating without melting. It forms insoluble salts with chlorides, bromides, iodides, and sulfides. Its nitrate is soluble. The *sodium compound* is made by pouring a solution in sodium hydroxide into alcohol.

The dimercurated saligenin is purified by repeated extractions with hot water, alcohol, and ether. It is then dried at 100° (Hg). The anhydride is believed to be formed by the elimination of water between the phenolic hydroxyl and the — HgOH group ortho to it. When air dried it contains 3.5 H_2O. (Hg).

The anhydride reacts with hot acetic anhydride giving a *triacetate* which probably has acetate groups on the two mercury atoms and on the alcohol group. (Hg). The phenolic hydroxyl is not acetylated.

[127] Balbiano, loc. cit.

[128] Balbiano, *Ber.* 42 (1909), 1506.

[129] Manchot, *Ann.* 421 (1920), 329.

[130] Hart and Hirschfelder, *J. Am. Chem. Soc.* 42 (1920), 2680.

Mercury Derivatives of p-Hydroxy-m-Nitrobenzyl Alcohol.[131]

3-Hydroxymercuri-4-hydroxy-5-nitrobenzyl alcohol.

The substituted carbinol is refluxed with alcoholic mercuric acetate and a little acetic acid. After cooling, the solution deposits yellow crystals. The product is only slightly soluble in water and is insoluble in common solvents. It dissolves completely in sodium hydroxide except for a trace of mercurous compound. The alkaline solution has a deep reddish yellow color. It can be crystallized from hot glacial acetic acid or acetic anhydride. It does not melt at 240°. An aqueous suspension does not react with hydrogen sulfide. A solution in sodium hydroxide reacts slowly with hydrogen sulfide giving mercuric sulfide. It gives the following insoluble salts, chloride, bromide, iodide, and sulfate. The nitrate is soluble.

The mercury compound is purified for analysis by crystallizing three times from 20 per cent acetic acid. Beautiful long light yellow crystals separate. (Hg). The fact that the substance does not lose water to form an inner anhydride when heated at 110° is used as evidence that the —HgOH group is in position 2, that is, *meta* to the phenolic hydroxyl. Such an orientation of the mercury is entirely improbable.[132] Treatment with hot acetic anhydride gives a monoacetate (Hg). The acetate group is probably attached to the mercury. If that is the case the acetate is *3-Acetoxymercuri-4-hydroxy-5-nitrobenzyl alcohol.*

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[131] Hart and Hirschfelder, *J. Am. Chem. Soc.* 42 (1920), 2683.

[132] The position of the mercury has been proved to be ortho to the hydroxyl group by treating the mercury compound with iodine in potassium iodide solution. The product is 3-iodo-4-hydroxy-5-nitrobenzyl alcohol. Oxidation changes this to the corresponding benzoic acid. Kharasch, *J. Am. Chem. Soc.* 43 (1921), 1203.

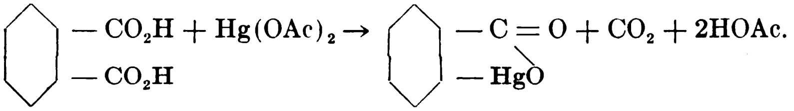
Chapter XII.

Mercury Derivatives of Aromatic Acids.

Mercury Derivatives of Benzoic Acid.[1]

Anhydride of o-hydroxymercuri benzoic acid.

Pesci originally thought that the product of the mercuration of benzoic acid had the mercury in the para position. The fact that it is in the ortho position was proved by Dimroth and confirmed by Pesci by making the mercurated benzoic acid from phthalic acid and mercuric acetate with the elimination of CO_2.[2]



Preparation.

1. Anhydrous mercuric benzoate is heated in an oil bath at 170° until a sample dissolves in sodium hydroxide. The resulting product is a mixture of the C — Hg compound and free benzoic acid. The latter is washed out of the mixture by alcohol and ether. The residue is dissolved in the least possible dilute sodium carbonate solution. The pure anhydride is then precipitated by passing carbon dioxide into the solution.

2. Benzoic acid is fused with mercuric acetate until the reaction is complete. The melt is cooled, powdered and dissolved in ammonium hydroxide, filtered, and boiled with sodium carbonate for two hours. The solution is filtered, cooled, and treated with carbon dioxide to

[1] Dimroth, *Ber.* 32 (1899), 765. *Chem. Zentr.* 1899 I 936. Pesci, *Atti. accad. Lincei* (5) 9 I (1900), 255. *Chem. Zentr.* 1900 I 1097. Dimroth, *Chem. Zentr.* 1901 I 449. Pesci, *Atti accad. Lincei* (5) 10 I (1900), 362. *Chem. Zentr.* 1901 II 108. Sand and Singer, *Ber.* 35 (1902), 3170. Dimroth, *Ber.* 35 (1902), 2872. Pesci, *Gazz. chim. ital.* 32 II (1902), 280. *Chem. Zentr.* 1902 I 1454. D. R. P. 229,574. *Chem. Zentr.* 1911 I 275. D. R. P. 229,781. *Chem. Zentr.* 1911 I 276. Sachs, *Ber.* 53 (1920), 1740,

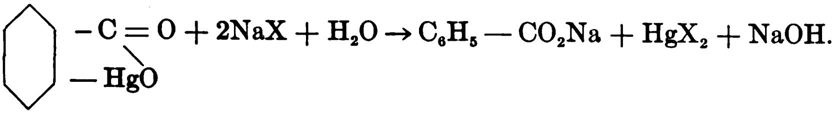
[2] Pesci, *Atti accad. Lincei* (5) 10 I (1901), 362.

precipitate the anhydride. This is dissolved in ammonium carbonate solution which is then precipitated by an excess of acetic acid.

3. When a solution of sodium phthalate is boiled with mercuric acetate and a little acetic acid carbon dioxide is evolved and the anhydride is precipitated.

Properties.

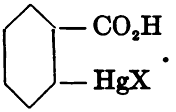
White poorly crystalline powder, almost insoluble in all common solvents, soluble in solutions of alkalies and alkaline carbonates. It is fairly stable to mineral acids forming salts of the type $\left[\begin{matrix}-CO_2H\\-HgX\end{matrix}\right.$. Sodium hydroxide gives a salt, $\left[\begin{matrix}-CO_2Na\\-HgOH\end{matrix}\right.$. Salts like sodium chloride form the third type of salt, $\left[\begin{matrix}-CO_2Na\\-HgCl\end{matrix}\right.$. All these salts have a strong tendency to hydrolyze and are therefore hard to prepare in the pure state. Boiling with an excess of an inorganic halide tends to split the $C-Hg$ linkage forming a benzoate and a molecule of free base.



$$-C=O + 2NaX + H_2O \rightarrow C_6H_5-CO_2Na + HgX_2 + NaOH.$$

The splitting effects of the halides decrease from the iodide to the chloride. Excess of mineral acids gives benzoic acid and mercuric salts. Bromine forms ortho bromobenzoic acid. Thionyl chloride gives a 60 per cent yield of o-chloromercuribenzoyl chloride.

Salts of the type,

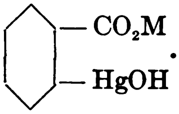


Salts of this type may be made by treating the anhydride with a slight excess of the proper dilute acid. They can also be made by adding the salt NaX and acidifying with dilute acetic acid. These salts, as a rule, are only sparingly soluble in water and alcohol. Salts have been prepared in which $X = Cl$, Br, I, S, and $-SC_2H_5$. The salts have no melting points. In general their reactions have not been studied. Thionyl chloride gives very little action with o-chloromercuribenzoic acid. This same substance reacts with ethyl mercaptan at

150° to form benzoic acid and ethyl mercaptide mercuric chloride, $C_2H_5 - S - HgCl$.[3]

o-Ethylmercaptomercuribenzoic acid reacts with thionyl chloride to give the $-HgCl$ compound.[4] The sulfide $(RHg)_2S$ when heated gives mercuric sulfide and mercuribis-o-benzoic acid.[5]

Salts of the type,



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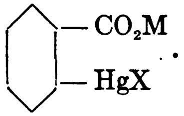
This type of salt is made by dissolving the anhydride in a solution of the base or by treating such a solution with a salt of the desired metal. These salts, as a general rule, are more soluble than the preceding type. Salts have been made in which $M = NH_4$, Ba, Ca, Mg, Ag, isoamylammonium and benzylammonium. Other salts have been made in solution but cannot be isolated.[6]

Salts of the type,



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These salts are made by treating the anhydride with a solution of MX. They are rather more stable than the salts of the second type. When $X = Cl$ salts have been made with $M = Na$, K, NH_4, Ba, and phenylammonium. With $X = Br$, $M = Na$, K, and Ba. With $X = I$, $M = Na$, K, and Ba. When $X = S$, $M = Na$ and K. Other salts have been obtained in solution. The sodium salt of o-chloromercuribenzoic acid reacts with ethyl mercaptan in the cold forming o-mercaptomercuribenzoic acid. This is in sharp contrast to the action of the free acid which gives no reaction up to 150° and then only with the splitting of the $C - Hg$ linkage.

Mercury Derivatives of Benzoic Ester.[7]

o-Chloromercuribenzoic methyl ester.[8]

Benzoic ester does not react with mercuric acetate in the cold even on standing for months. When powdered mercuric acetate is refluxed

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[3] Sachs, loc. cit. 1743.

[4] *Ibid.* 1745.

[5] Pesci, *Gazz. chim. ital.* 32 II (1902), 292. *Chem. Zentr.* 1902 II 1454.

[6] D. R. P. 261,875. *Chem. Zentr.* 1913 II 395.

[7] Schoeller and Hueter, *Ber.* 47 (1914), 1932. Schoeller and Schrauth, *Ber.* 53 (1920), 636. Sachs, *Ber.* 53 (1920), 1739.

[8] Schoeller and Schrauth, loc. cit.

with methyl benzoate and a small amount of acetic acid for four hours a side test shows no more mercuric ions. A small amount of mercurous acetate and mercury has to be filtered off. Evaporation of the filtrate in a vacuum leaves a yellow oil. When acetone is added about one-quarter of the oil is precipitated as an amorphous solid. The mercury content corresponds to a di-acetoxymercuribenzoic ester. Evaporation of the acetone solution leaves a slightly yellow resin. When this is dissolved in water and treated with sodium chloride solution a precipitate of chloromercuribenzoic methyl ester is obtained. This is purified by dissolving it in ethyl acetate and precipitating it with low boiling ligroin. (CHHgCl). It is fairly soluble in alcohol, ethyl acetate, chloroform, less in ether, practically insoluble in low boiling ligroin and water. It sinters 142°, melts 162°. Ammonium sulfide gives HgS only on long warming. This chloride has also been made by boiling sulfidemercuribenzoyl chloride with methyl alcohol. Prepared in this way it has a melting point of 182°.[9] Since the benzoyl chloride was made from the mercury benzoic anhydride which is known to have the mercury in the ortho position the proof of the identity of these two chloromercuribenzoic esters would confirm the assumption that the mercuration of benzoic ester goes in the same way as that of benzoic acid.

Sulfidemercuribenzoic methyl ester. $S(—Hg—C_6H_4—CO_2CH_3)_2$.[10]

The chloride is dissolved in warm methyl alcohol and cooled and treated with one-half mole of a methyl alcohol solution of hydrogen sulfide. An amorphous white precipitate is formed. An excess of hydrogen sulfide must be avoided as it dissolves the precipitate. The precipitate is filtered at once as it turns yellow on standing in the mother liquor. It forms a white amorphous powder, which blackens on heating. (SHg). It is slightly soluble in alcohol, ethyl acetate, acetone, ether, and low boiling ligroin, easily soluble in chloroform, benzene, and aniline. All of these solutions slowly darken. It is soluble in excess of hydrogen sulfide or sodium sulfide solutions apparently forming soluble compounds containing the groupings — HgSH and — HgSNa.

[9] Sachs, loc. cit. 1741.

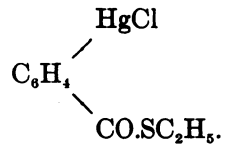
[10] Schoeller and Schrauth, loc. cit. 637.

o-Mercuribis-(benzoic methyl ester).[11]

The sulfide is heated 3 hours at 120°. The residue is cooled and extracted with ethyl acetate leaving HgS behind. Spontaneous evaporation of the extracts gives white crystals in 90 per cent yield. These are recrystallized from alcohol and ether. (CHHg). It does not react with sodium stannite. It is soluble in methyl and ethyl alcohol, acetone, ethyl acetate, chloroform, benzene, difficultly soluble in water and ligroin. Saponification gives mercuribis-(benzoic acid).

o-Chloromercuribenzoyl chloride.[12]

The pure anhydride is treated with an excess of thionyl chloride. The reaction starts instantly. The precipitate is washed with chloroform. It consists of needle crystals and an amorphous substance. Extraction with benzene leaves most of the latter substance undissolved. M.P. 173.5° (not complete) (ClHg). When dissolved in ether and treated with dry hydrogen sulfide it gives o-sulfidemercuribenzoyl chloride, $S(HgC_6H_4—COCl)_2$, a slightly yellow precipitate which does not melt at 230°. It reacts with concentrated hydrochloric acid giving hydrogen sulfide. It does not react with mercuric oxide, showing that it does not contain the grouping —CO.S —. (CHSHg). When boiled with methyl alcohol it gives HCl, HgS, methyl benzoate, and o-chloromercuribenzoic methyl ester. When chloromercuribenzoyl chloride is refluxed with methyl mercaptan in benzene solution it gives chloromercurithiobenzoic ethyl ester.



$$C_6H_4\begin{cases}HgCl\\ CO.SC_2H_5.\end{cases}$$

This substance forms slightly yellow rhombic leaflets, soluble in alcohol, ether, benzene, chloroform, and acetone. (CH).

o-Mercuribis-benzoic acid.[13]

Preparation.

1. A solution of the sodium salt of o-hydroxymercuribenzoic acid is precipitated by the calculated amount of sodium sulfide. Long

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[11] *Ibid.*

[12] Sachs, loc. cit.

[13] Pesci, *Atti accad. Lincei* (5) 10 I (1901), 413. *Chem. Zentr.* 1901 II 108. *J. Chem. Soc.* 80 (1901), 624. *Gazz. chim. ital.* 32 II (1902), 293. Schoeller and Schrauth, loc. cit. 638.

boiling of the mixture gives mercuric sulfide and a solution of the sodium salt of o-mercuribis-benzoic acid. This can be precipitated as the calcium salt, then changed to the pure sodium salt by sodium carbonate and finally acidified with acetic acid to precipitate the pure acid. This forms needles from hot alcohol, insoluble in water. It decomposes on heating without melting. Several salts have been made and analyzed.

2. By the saponification of o-mercuribis-benzoic ester by alcoholic sodium hydroxide.[14] (CHHg). It is soluble in alcohol, chloroform, and hot water.

Miscellaneous references on mercury benzoic acid compounds.[15]

Mercury Derivatives of Substituted Benzoic Acids.

Anhydride of o-hydroxymercuri-o′-chlorobenzoic acid.[16]

The anhydride is made by heating the mercury salt of the acid to 140° until the substance is alkali soluble. It is insoluble in water, alcohol, and ether. With glutarimide it forms a crystalline compound which is water soluble. With sodium hydroxide it gives a soluble salt.

The sodium salt of *m-chlorobenzoic acid* heated with mercuric acetate in water gives a white powder which is soluble in sodium chloride solution.[16a] It gives a yellow precipitate with sodium hydroxide.

The anhydride of *2-hydroxymercuri-3, 5-dibromobenzoic acid.*[17]

The anhydride of *o-hydroxymercuri-o-iodobenzoic acid.*[18]

The anhydride of *o-hydroxymercuri-o′-nitrobenzoic acid*[19] is obtained by heating the mercury salt of o-nitrobenzoic acid at 200°. If this compound is reduced in alkaline or neutral medium by one equivalent of hydrogen for each mole of the anhydride it gives *o-mercuribis-o′-nitrobenzoic acid.* If the reduction is carried further the corresponding amino compound is obtained.

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[14] Schoeller and Schrauth, *ibid.*

[15] Schoeller and Schrauth, *Biochem. Z.* 32 (1911), 511. Schoeller and Schrauth and Müller, *Biochem. Z.* 33 (1911), 403. Schoeller and Schrauth, D. R. P. 248,291. *Chem. Zentr.* 1912 II 211. *Chem. Abst.* 8 (1914), 21, 231. D. R. P. 249,332. *Chem. Zentr.* 1912 II 465. D. R. P. 234,914. Fränkel, *Die Arzneimittelsynthese,* 1919, p. 665. Devillers, *Chem. Abst.* 7 (1913), 1580.

[16] D. R. P. 229,574. *Chem. Zentr.* 1911 I 275. Schrauth, *Seifensieder Ztg.* 37 (1910), 1276, 1323. *Chem. Zentr.* 1911 I 695. D. R. P. 234,914. *Chem. Zentr.* 1911 II 112. D. R. P. 234,054. Fränkel, p. 665.

[16a] Private communication, G. W. Raiziss.

[17] D. R. P. 249,332. Fränkel, p. 665. *Chem. Zentr.* 1912 II 465.

[18] D. R. P. 234,914. Fränkel, p. 665. *Chem. Zentr.* 1911 II 112.

[19] D. R. P. 251,332. Fränkel, p. 670. D. R. P. 249,725, *ibid.*

m-Nitrobenzoic acid when heated with mercuric acetate gives products containing one and two atoms of mercury. The position of the mercury groups has not yet been determined.[20] Heating the mercuric salt of m-nitrobenzoic acid gives two products each containing one atom of mercury.[21] One still contains a carboxyl group and is soluble in alkali. The other has lost a molecule of carbon dioxide and is insoluble in alkali.

The anhydride of *o-hydroxymercuri-p-nitrobenzoic acid*[22] is obtained by heating the mercury salt of p-nitrobenzoic acid at 200°. It can be reduced by stannous chloride or ferrous hydroxide to *o-mercuribis-p-nitrobenzoic acid.* This is a yellow powder which is decomposed by heat giving an odor of nitrobenzene. It is soluble in alkalies. The concentrated solution in sodium hydroxide when treated with alcohol gives a disodium salt as a yellow flocculent precipitate. The sodium salt is soluble in water. Its solution gives precipitates with solutions of heavy metal salts. Further reduction in neutral or alkaline solution gives *o-mercuribis-p-aminobenzoic acid.*

Derivatives of sym-dinitrobenzoic acid.[23]

The *anhydride* is made in the usual way. When reduced by stannous chloride or ferrous hydroxide it yields *2, 2'-mercuribis-3, 5 dinitrobenzoic acid,* a yellow powder insoluble except in solutions of bases. Its disodium salt is a crystalline yellow powder.

Derivatives of Anthranilic Acid.[24]

N-iso di-acetoxymercuri anthranilic methyl ester,

$$AcOHg - C_6H_3(CO_2Me) - NH - HgOAc.H_2O.$$

Equal molecules of methyl anthranilate and mercuric acetate are mixed in 80 per cent methyl alcohol. In a few minutes a white flocculent precipitate fills the solution. After 1.5 hours a sample gives no mercuric oxide with sodium hydroxide. The water of crystallization

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[20] Unpublished results, Whitmore and V. E. Meharg.

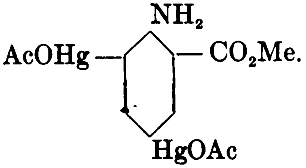
[21] Private communication, M. S. Kharasch.

[22] Blumenthal and Oppenheim, *Biochem. Z.* 32 (1911), 60; 35 (1911) 505; 39 (1912), 54, 58; 57 (1913), 277; 65 (1914), 461. D. R. P. 251,332. *Chem. Zentr.* 1912 II 1413. D. R. P. 249,725. *Chem. Abst.* 6 (1912), 1467.

[23] D. R. P. 251,332 loc. cit.

[24] Schoeller and Hueter, *Ber.* 47 (1914), 1930. Schoeller, Schrauth, and Liese, *Ber.* 52 (1919), 1777. Schoeller and Schrauth, *Ber.* 53 (1920), 634.

cannot be removed even at 75° in a vacuum without decomposition. (CHHg). On standing in the mother liquor containing the unused methyl anthranilate the amorphous precipitate changes completely to slightly yellow needle crystals of the acetoxymercuri anthranilic ester. The "N-isodiacetate" is soluble in acetic acid. If this solution is neutralized with ammonium hydroxide and treated with ammonium sulfide, one-half of the mercury is precipitated as mercuric sulfide. Cold dilute hydrochloric acid changes the "N-iso diacetate" to mercuric chloride and chloromercuri anthranilic ester. In each of these reactions the N — Hg linkage is broken while the C — Hg is left intact. It is also soluble in hot water, hot methyl and ethyl alcohols, almost insoluble in acetone, chloroform, benzene, and low boiling ligroin. The hot aqueous or alcoholic solution on cooling forms a jelly. The "N-iso diacetate" dissolved in methyl alcohol and heated for half an hour with an acetic acid solution of methyl anthranilate gives crystals of acetoxymercuri anthranilic ester, in almost quantitative yield. If the "N-iso diacetate" is heated alone with acetic acid and methyl alcohol for half an hour at 50° it gives diacetoxymercuri anthranilic methyl ester.



Acetoxymercuri anthranilic methyl ester.

The "N-iso diacetate" is suspended in methyl alcohol and heated with the calculated amount of methyl anthranilate dissolved in a little acetic acid. Solution is complete after heating half an hour at 50°. Crystals soon begin to separate. After standing in ice for 24 hours the mixture is filtered. M.P. 178-80° (corr. 180-182°). A better method of making the compound is to treat methyl anthranilate with one mole of mercuric acetate in methyl alcohol and acetic acid at 50°. The reaction is complete in about 15 minutes as is shown by a side test with ammonium sulfide. On cooling, yellow needles separate. Yield 90% (CHNHg). It is easily soluble in boiling water, hot methyl or ethyl alcohol, ammonium hydroxide, acetic acid, more difficultly in benzene, ethyl acetate, and acetone, very little in chloroform. It gives no action with ammonium sulfide.

Chloromercuri anthranilic methyl ester.

The acetate in alcohol solution is mixed with a dilute solution of sodium chloride. It forms small needles, soluble in the usual organic solvents especially in ethyl acetate from which it may be precipitated by petrol ether. M.P. 182° (corr. 184°) (ClHg). The corresponding *bromide* is made in the same way. It forms fine white needles when recrystallized from water. M.P. 178° (BrHg). The *iodide* is made in the same way. Recrystallized from alcohol it forms small needles. M.P. 171-2° (corr. 173-4°). (IHg).

Anhydride of *2-amino-5-hydroxymercuri-benzoic acid.*

The acetate of the mercurated ester is suspended in water and treated with 2.25 moles of normal sodium hydroxide. Solution takes place on boiling. After cooling the solution is treated with 1.25 equivalents of normal sulfuric acid which forms a white flocculent precipitate. An excess of acid dissolves the precipitate. M.P. 212-214° (decomp.) (CHNHg). It is easily soluble in water solutions of potassium iodide, potassium cyanide, and sodium thiosulfate, less soluble in potassium bromide and still less in potassium chloride. It is very little soluble in organic solvents. It dissolves easily in ammonium hydroxide, ammonium carbonate, dilute sodium hydroxide and sodium carbonate solution. An ammonium hydroxide solution treated with ammonium sulfide gives no HgS until heated or after long standing. Another method of making the anhydride is by heating pure anthranilic acid with freshly prepared mercuric oxide and water. The heating is best done by a vigorous jet of steam passed into the suspension. The reaction is complete when a sample dissolves in alkali. The solid is dissolved in 1.25 moles of sodium hydroxide, filtered, and precipitated by an equivalent amount of sulfuric acid. Yield 96%. Decomp. 210° (CHNHg).

The anhydride reacts with iodine dissolved in potassium iodide solution giving an iodoanthranilic acid melting at 210.5°, with decomposition, showing that the mercury occupied the position para to the amino group. A solution of the anhydride in sodium hydroxide can be used to make various heavy metal salts by precipitation. The copper salt is a light green amorphous substance. (Cu).

Iodomercuri-anthranilic acid.

The anhydride is dissolved in potassium iodide solution. The dark brown solution is filtered from a small amount of yellow green residue.

The filtrate is diluted and treated with the calculated amount of .1 N sulfuric acid. An excess of acid splits mercuric iodide from the compound. (CHNHgI). It is very difficultly soluble in water and organic solvents, easily soluble in alkalies, decomposed by dilute acids.

Diacetoxymercuri-anthranilic methyl ester.

Prepared from anthranilic methyl ester and 2 moles of mercuric acetate in methyl alcohol and acetic acid heated one hour at 50°. The crystals obtained contain a trace of mercurous acetate. It is recrystallized from methyl alcohol and a small amount of acetic acid. (CHHg). M.P. 218-220° (corr. 221-222°), decomp. It is soluble in organic solvents but less so than the monomercury compound. The compound can also be made by heating the "N-iso diacetate" with acetic acid and methyl alcohol at 50°.

Anhydride of dihydroxymercuri-anthranilic acid.

The diacetate is suspended in water and treated with 3.25 moles of normal sodium hydroxide. The boiled solution is cooled and treated with 1.25 equivalents of normal sulfuric acid. A slightly yellow green amorphous precipitate separates. Poor analysis for CHHg. The substance could not be purified.

5, 5′-Mercuribis-2-aminobenzoic methyl ester,

$$Hg[C_6H_3(CO_2Me)-NH_2]_2.$$[25]

The acetate is dissolved in the least amount possible of 75 per cent alcohol and treated with a concentrated solution of sodium thiosulfate. An amorphous white precipitate forms at once. After standing 1.5 hours at 45° the mixture is evaporated in a vacuum and the residue is extracted with ethyl acetate, filtered, evaporated, and treated with low boiling ligroin to form a slight turbidity. On cooling light yellow needles form. Yield 65 per cent. (CHNHg). It is easily soluble in methyl and ethyl alcohols, ethyl acetate, acetone, chloroform, benzene, difficultly soluble in ligroin and water. M.P. 196-7° corr., after slight darkening.

6, 6′-Mercuribis-2-aminobenzoic acid.[26]

It is prepared by neutral or alkaline reduction of the anhydride or salts of *6-hydroxymercuri-2-nitrobenzoic acid.*[27]

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[25] Schoeller and Schrauth, *ibid.* 642.

[26] D. R. P. 249,725. Fränkel, 670.

[27] Blumenthal and Oppenheim, *Biochem. Z.* 57 (1913), 288; 65 (1914), 460.

Derivatives of acetyl anthranilic acid.[28]

Acetoxymercuri acetyl anthranilic methyl ester,

$$AcOHg — C_6H_3(CO_2Me) — NH — COCH_3.$$

In sharp contrast to anthranilic ester the acetylated compound must be refluxed for some time with mercuric acetate solution to complete the reaction. Even then only a monomercurated compound is obtained. When the two substances stand in cold alcoholic solution for 1.5 days only one-tenth of the mixture has reacted. Refluxing for two hours in water solution or for seven hours in methyl alcohol completes the reaction. Another and more rapid preparation is from the two substances heated without any solvent at 120-130° for half an hour. Any unchanged ester is extracted with ether and the mercury compound is recrystallized from dilute alcohol in which it is very soluble. The mercury compound remaining in the mother liquors can be precipitated as the chloride by means of sodium chloride. (CHNHg). It forms large plates from dilute alcohol, which are very soluble in organic solvents except ether and ligroin. M.P. 210° (corr. 212°).

Chloromercuri acetyl anthranilic methyl ester.

The mother liquors from the crystallization of the acetate from dilute alcohol are precipitated by dilute sodium chloride. It is recrystallized from ethyl acetate. (CHHg). It is little soluble in common solvents, best in hot ethyl acetate from which it forms fine needles. On rapid heating it melts at 245-6°.

Sodium salt of 2-hydroxymercuri-5-acetaminobenzoic acid.[29]

It is prepared from the corresponding anhydride by sodium hydroxide.

Derivatives of Alkylanthranilic Acids.

Acetoxymercuri methylanthranilic methyl ester,[30]

$$AcOHg — C_6H_3(CO_2Me) — NHCH_3.$$

Methylanthranilic methyl ester reacts about as rapidly with mercuric acetate as does the unmethylated ester but no intermediate N — Hg compound and no di-acetoxymercuri compound can be ob-

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[28] Schoeller and Hueter, *Ber.* 47 (1914), 1946. Fränkel, *Die Arzneimittelsynthese,* 1919, p. 669. D. R. P. 234,054. Fränkel, 665.

[29] Fränkel, 665 and 669. Blumenthal and Oppenheim, *Biochem. Z.* 57 (1913), 260.

[30] Schoeller and Hueter, loc. cit. 1940. Schoeller and Schrauth, D. R. P. 248,291. *Chem. Zentr.* 1912 II 211. Fränkel, 662.

tained. In methyl alcohol solution all mercuric ions disappear after one-half hour in the cold. Yield 97 per cent. It is recrystallized from methyl alcohol. (CHNHg). M.P. 198° (corr. 200°), decomp. It is very easily soluble in chloroform and hot acetic acid, easily soluble in boiling methyl and ethyl alcohols, ethyl acetate, acetone and benzene, only slightly soluble in boiling water. It forms needles from alcohol.

Chloromercuri methylanthranilic methyl ester.

It is prepared from the acetate and crystallizes from alcohol in white needles. M.P. 210-212°, turning violet. (ClHg). The corresponding *bromide* is made in the same way and crystallizes from ethyl acetate in which it is fairly soluble even in the cold. M.P. 215°, turning violet. (BrHg). The *iodide* is similar to the bromide. M.P. 190-191°, after turning brown. (IHg).

Anhydride of hydroxymercuri methylanthranilic acid.

It is prepared from a suspension of the acetate treated with sodium hydroxide and sulfuric acid in the usual way, as a greenish yellow amorphous precipitate. It decomposes without melting at 203° (CHNHg). The anhydride can also be prepared by boiling a solution of methylanthranilic acid with mercuric oxide. This reaction is rapid, going to completion in about fifteen minutes. Anthranilic acid itself requires three hours for the completion of this reaction. The anhydride is soluble in potassium iodide solution.

Iodomercuri methylanthranilic acid.

It is prepared from the anhydride by dissolving in potassium iodide solution, filtering off the slight solid residue, diluting and neutralizing with sulfuric acid. It is soluble in alkalies but is more stable to acids than the corresponding compound containing a free NH_2 group. It is practically insoluble in all organic solvents. (CHNHgI).

Acetoxymercuri ethylanthranilic ethyl ester,[31]

$$AcOHg — C_6H_3(CO_2Et) — NH — C_2H_5.$$

The reaction between the ester and mercuric acetate in methyl alcohol is complete in an hour and a half. It crystallizes from methyl alcohol in needles. (CHNHg). M.P. 176° (corr. 178°), decomp. It is easily soluble in hot organic solvents, only slightly soluble in boiling

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[31] Schoeller and Hueter, loc. cit. 1943.

water. The corresponding mercurated *methyl* ester of ethylanthranilic acid is made in the same way and has similar properties. On rapid heating it melts at 187° (corr. 189°) (Hg).

Acetoxymercuri dimethylanthranilic methyl ester,[32]

$$AcOHg — C_6H_3(CO_2Me) — N(CH_3)_2.$$

Prepared in the usual way in methyl alcohol. The reaction is complete in three hours. 77% yield. Prismatic crystals. It is crystallized from methyl alcohol. M.P. 133° (corr. 134°). It is easily soluble in organic solvents.

Chloromercuri dimethylanthranilic methyl ester.

It is prepared from the acetate and recrystallized from methyl alcohol. It forms white needles which gradually change to prisms. The first crystals contain 1 H_2O. (ClHg). M.P. 162-3°. The *bromide* is made like the chloride. White needles M.P. 164°. The crystals contain 1 H_2O. (H_2O,Hg). The water is lost at 100° in vacuum. (BrHg). The *iodide* forms white needles from methyl alcohol. These gradually change to prisms. M.P. 159° (IHg).

Sulfatemercuri dimethylanthranilic acid.

This sulfate is obtained when an attempt is made to make the anhydride from the acetate by the usual method of saponifying by sodium hydroxide and acidifying with normal sulfuric acid. In this case the sulfate precipitates instead of the anhydride. The precipitate is at first slimy but becomes crystalline on standing. It can be crystallized from alcohol in needles. It decomposes slowly at 180° (CHHgS). It is almost insoluble in organic solvents, easily soluble in hot water. The corresponding *chloride* is obtained from the saponification mixture by acidifying with normal hydrochloric acid instead of sulfuric acid. On rapid heating it melts with decomposition at 175°. It is very easily soluble in boiling water, fairly in cold, difficultly soluble in most organic solvents.

The diethyl ester of o-carboxylphenylamino acetic acid reacts with mercuric acetate giving only a mono mercury compound.[33]

$$AcOHg — C_6H_3(CO_2Et) — NH — CH_2CO_2Et.$$

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[32] *Ibid.*

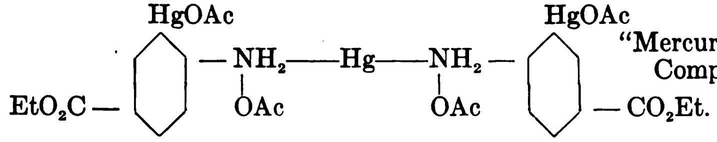
[33] J. Rother, *Dissert.* Berlin, 1911, pp. 18 and 53.

Derivatives of acylated m-aminobenzoic acids.[34]

Heating the corresponding mercury salts gives the anhydrides of *2-hydroxymercuri-5-acetaminobenzoic acid,* and the corresponding *benzoylamino compound.*

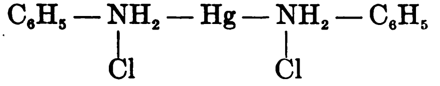
Derivatives of p-aminobenzoic acid.[35]

The ethyl ester of p-aminobenzoic acid reacts with mercuric acetate in methyl alcohol much as does the ester of anthranilic acid. It forms the corresponding "N-isodiacetate." This changes on heating into the true organic di-acetoxymercuri compound but differs from the anthranilic compound in that it does this even in presence of an excess of the original ester. Thus in the case of the p-compound further mercuration of the same molecule is easier than the transfer of the —HgOAc group to a molecule of unmercurated ester while the reverse is true in the case of the ortho compound. This conclusion may be erroneous as the difference might be due to the difference between the methyl and ethyl esters used. The reaction of the p-compound differs also in that an excess of the ester gives a compound in which one mercury atom is linked to two nitrogen atoms each of which has a molecule of acetic acid added to it making it quinquevalent. This compound may be regarded as a mercuric acetate "salt" of a mercurated substituted aniline,



"Mercury-N-iso" Compound.

This would correspond to the commonest mercuric "salt" of aniline,



$$\underset{\displaystyle Cl}{C_6H_5 - NH_2} - Hg - \underset{\displaystyle Cl}{NH_2 - C_6H_5}$$

N-iso diacetoxymercuri-p-aminobenzoic ethyl ester,

$$AcOHg - C_6H_3(CO_2Et) - NH - HgOAc.$$

This substance is obtained as a yellow amorphous mass by allowing the ethyl ester to stand with 2 moles of mercuric acetate in methyl alcohol for a day. The substance cannot be recrystallized. (CHNHg).

[34] D. R. P. 264,388. Fränkel, 668.

[35] Schoeller, Schrauth, and Liese, *Ber.* 52 (1919), 1782.

M.P. about 245°. It is soluble in ammonium hydroxide, acetic acid, and is decomposed by mineral acids. It is practically insoluble in organic solvents. It reacts in the cold with ammonium sulfide. The acetic acid solution when treated with sodium chloride loses one-half of its mercury as mercuric chloride leaving *chloromercuri-p-aminobenzoic ester.* When warmed with acetic acid it gives diacetoxymercuri-p-aminobenzoic ethyl ester, $(AcOHg)_2C_6H_2(CO_2Et) — NH_2$.

This reaction takes place even in the presence of an excess of the free ester (contrast the o-compound). If boiled with methyl alcohol and acetic acid and sodium chloride solution it gives a 94% yield of chloromercuri-p-aminobenzoic ester. The filtrate when treated with ammonium hydroxide and hydrogen sulfide gives mercuric sulfide corresponding to one-half of the mercury in the original compound. Another method of making the N-iso di-acetoxymercuri compound is to boil the mercuric acetate "salt" with methyl alcohol. This precipitates the N-isodiacetate in 72% yield. The latter substance when treated with sodium chloride solution and hydrogen sulfide loses one-half of its mercury as mercuric sulfide.

Mercuric acetate salt of acetoxymercuri-p-aminobenzoic ethyl ester. ("Mercury-N-iso" compound. See above formula.)

It is prepared from equivalent amounts of the ester and mercuric acetate allowed to stand in methyl alcohol. It forms microscopic diamond shaped crystals. M.P. 230-240°. Analysis (CHNHg,HOAc) distilled off over phosphoric acid . It dissolves in ammonium hydroxide and acids with decomposition, dissolves a little in cold methyl alcohol, acetone, and ethyl acetate. It reacts with cold ammonium sulfide. Boiling with methyl alcohol gives a precipitate of the "N-isodiacetate" and a solution of acetoxymercuri-p-aminobenzoic ethyl ester. The mother liquor contains two moles of acetic acid.

When the "Mercury-N-iso" compound is boiled with acetic acid and then heated in a vacuum to drive off the acetic acid, it leaves a residue which is partly soluble in methyl alcohol. The methyl alcohol solution treated with sodium chloride gives chloromercuri-p-aminobenzoic ethyl ester. The insoluble residue is extracted with ethyl acetate giving di-acetoxymercuri-p-aminobenzoic ester. The final insoluble portion consists of traces of mercurous acetate. When the "Mercury-N-iso" compound is treated with methyl alcohol, acid and sodium chloride, it gives chloromercuri-p-aminobenzoic ester. The mother liquor treated with ammonium sulfide gives an amount of mercuric sulfide corresponding to one-third of the mercury originally present in the compound.

Acetoxymercuri-p-aminobenzoic ethyl ester.[86]

It is prepared from equivalent amounts of the ester and mercuric acetate in warm acetic acid. The precipitate formed is extracted with methyl alcohol which dissolves the mono-mercurated product but leaves the di-product. It is not possible to get the mono compound pure by carrying out the reaction in acetic acid or methyl alcohol solution. The best method of preparation is to heat equivalent amounts of the ester and mercuric acetate without any solvent in a glycerine bath. At 130° the mixture melts and at a higher temperature acetic acid is given off. Finally the mixture solidifies to a cake at 160°. This is cooled, broken up, and extracted with hot methyl alcohol, evaporated and diluted with hot water. The acetate forms beautiful white clustered needles. The residue insoluble in methyl alcohol, is a partly acetylated di-acetoxymercuri compound. Analysis of mono-acetate, CHNHg. It melts partly at 182°, solidifies and again melts at 228°. It is soluble in most organic solvents, especially in methyl alcohol, ethyl acetate and chloroform. It is also soluble in dilute acetic acid and slightly in water, difficultly soluble in ether and low boiling ligroin. It is stable to ammonium sulfide forming a yellow sulfide which blackens only on long boiling. Another preparation is that already mentioned by heating the "Mercury-N-iso" compound with methyl alcohol. If the acetate is boiled with sodium hydroxide and the resulting solution is acidified there results the *anhydride* of hydroxymercuri-p-aminobenzoic. acid.

Chloromercuri-p-aminobenzoic ethyl ester.

It is prepared from the acetate by sodium chloride. M.P. 223°. It is difficultly soluble in common solvents. It is best purified by dissolving in ethyl acetate, and adding low boiling ligroin in which it is practically insoluble. (CHNClHg). It is stable to ammonium sulfide except on long boiling. The chloride can also be prepared by boiling the "N-iso" or the "Mercury-N-iso" compound with methyl alcohol and acetic acid and precipitating the resulting solution with sodium chloride.

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[86] Schoeller, Schrauth, and Liese, *Ber.* 52 (1919), 1784.

Anhydride of hydroxymercuri-p-aminobenzoic acid.[37]

The acetate of the corresponding ethyl ester is suspended in water and saponified by boiling with normal sodium hydroxide. The solution of the sodium salt is cooled and treated with a slightly more than the calculated amount of the normal sulfuric acid. An excess of acid will dissolve the anhydride. The precipitate formed is very insoluble in common solvents. It is soluble in ammonium hydroxide. This solution reacts with ammonium sulfide only on heating. It is soluble in water solutions of many salts such as sodium thiosulfate, potassium iodide and potassium chloride. It is also soluble in bases with salt formation. The anhydride has also been obtained by mercurating the isobutyl ester of p-aminobenzoic acid, saponifying the product, and acidifying.[38]

Diacetoxymercuri-p-aminobenzoic ethyl ester,

$$(AcOHg)_2C_6H_2(CO_2Et)-NH_2.$$

It is prepared from the ester and two molecules of mercuric acetate in acetic acid. After standing for two days a well crystallized product is obtained. The pure di-compound is obtained by washing this precipitate with methyl alcohol and ether. It is only slightly soluble in common solvents, but can be recrystallized from acetone or ethyl acetate in flat needles. M.P. 255-7°. The diacetate can also be prepared by boiling the "N-iso" or the "Mercury-N-iso" compound with acetic acid and diluting the solution. It is stable to ammonium sulfide even on gentle warming. (CHNHg). It can be acetylated by acetic acid and acetic anhydride forming *diacetoxymercuri-p-acetaminobenzoic ethyl ester.*

It is purified by recrystallization from dilute alcohol or by solution in acetic acid and dilution with hot water. Fine needles. (CHNHg). M.P. 247°.

Dichloromercuri-p-aminobenzoic ethyl ester.

It is prepared from the diacetate dissolved in acetic acid and methyl alcohol and precipitated by sodium chloride. Fine needle crystals not very soluble in ethyl acetate, soluble in acetone. M.P. 270° (CHHg).

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[37] *Ibid.* 1785.

[38] D. R. P. 248,291. *Chem. Zentr.* 1912 II 211. Friedländer, 10, 1278. Fränkel, 662.

3, 3'-Mercuribis-4-aminobenzoic ethyl ester.[39]

Chloromercuri-p-aminobenzoic ethyl ester is warmed with a concentrated solution of sodium thiosulfate. Most of the substance goes into solution. A precipitate soon starts to form. This dissolves well in ethyl acetate. It can be purified by dissolving in benzene and adding ligroin. Slightly yellow needles. M.P. 176° corr. (CHHg).

2, 2'-Mercuribis-4-aminobenzoic acid.[40]

Neutral or alkaline reduction of the anhydride or salts of the hydroxy-mercuri-p-nitrobenzoic acid obtained by heating the corresponding acid with mercuric oxide until the product is completely soluble in sodium hydroxide, gives this substance. The sodium salt is a yellowish white crystalline powder which is readily soluble in water. The free acid is precipitated by the addition of dilute hydrochloric acid to the solution of the sodium salt. Hydrogen sulfide gives no mercuric sulfide. It can be diazotized and coupled with an acid solution of alpha naphthylamine or with basic solutions of the naphthols. With the former it gives a blue violet color and with the two latter purple red solutions.

Animal experiments with salts of the above acid.[41]

The chart on page 308 will illustrate the relations between the mercuration products of the aminobenzoic acids.

Toluidoacetic esters. See under Toluidine.[42]

Sulfamido benzoic compounds.

The sodium compound of saccharin[43] reacts with mercuric salts giving N — Hg compounds of saccharin. These compounds react with bases, iodides, and sulfides giving the characteristic reactions of mercuric ions.

Salts of the mono- and di-sulfamido benzoic acids react with mercuric oxide or carbonate giving soluble compounds containing the grouping, $—SO_2—NH—HgOH$.[44]

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[39] Schoeller and Schrauth, *Ber.* 53 (1920), 643.

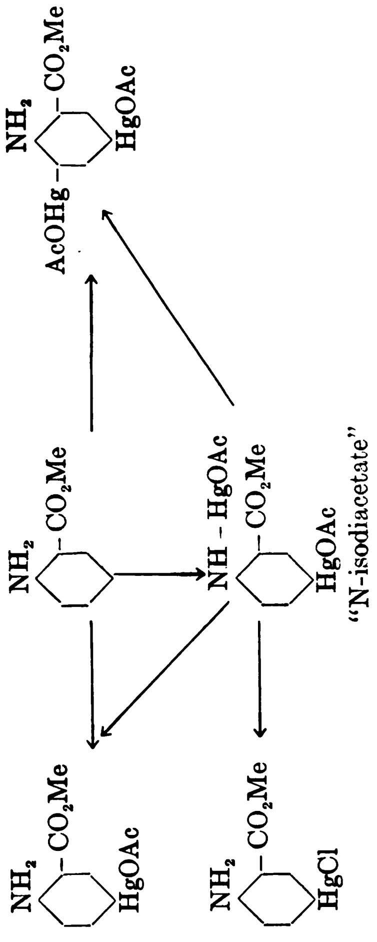
[40] Blumenthal, *Biochem. Z.* 32 (1911), 60. *Chem. Abst.* 6 (1912), 1466. D. R. P. 249,725. Fränkel, 670.

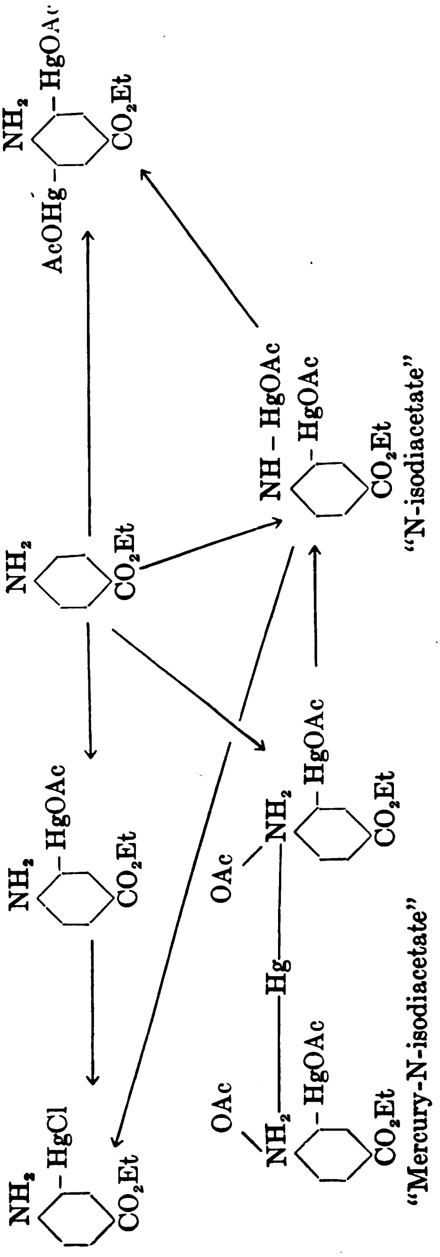
[41] Blumenthal and Oppenheim, *Biochem. Z.* 36 (1911), 295; 39 (1912), 53; 57 (1913), 287.

[42] J. Rother, loc. cit. 42.

[43] Dufournel, *Bull. soc. chim.* (3) 25 (1901), 326. Auld, *J. Chem. Soc.* 91 (1907), 1048.

[44] D. R. P. 242,571 and 242,572. *Chem. Zentr.* 1912 I 385.


NH₂
CO₂Me
AcOHg
HgOAc
NH - HgOAc
HgCl
"N-isodiacetate"


NH₂
CO₂Et
AcOHg
HgOAc
NH - HgOAc
HgCl
OAc
Hg
"N-isodiacetate"
"Mercury-N-isodiacetate"

These compounds react with ammonium sulfide. They form soluble compounds with 2 molecules of mercurisalicyl anhydride for each $-SO_2NH-Hg-HgOH$ group.

These solutions do not act on metals or albumen. What is more remarkable is that they do not react with ammonium sulfide except on boiling.[45]

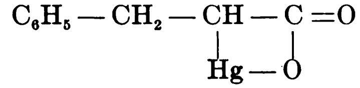
Benzosulfonic acids.[46]

Saccharine reacts with mercuric acetate in boiling water solution forming a mercury compound which is insoluble in acids and alkalies but is soluble in physiological salt solution.[46a]

Hydroxymercuri o-toluylic acid.[47]

The anhydride is obtained in the usual way by heating the acid with mercuric oxide until the product is alkali soluble.

Anhydride of α-hydroxymercuri-β-phenyl propionic acid.[47a]



$$\begin{array}{l} C_6H_5-CH_2-CH-C=O \\ \qquad\qquad\qquad\ \ |\qquad\ | \\ \qquad\qquad\qquad Hg-O \end{array}$$

The mercuric salt of benzylmalonic acid is heated to drive out one molecule of carbon dioxide. Treatment of the anhydride with the calculated amount of hydrochloric acid gives the *α-chloromercuri compound.*

Anhydride of 2-hydroxymercuri-3, 6-dimethylbenzoic acid.[48]

Anhydride of 2-hydroxymercuri trimethylbenzoic acid.[49]

Mercury Derivatives of Cinnamic Acid and Its Esters.

Common cinnamic acid gives no compound with mercuric salts from which all of the mercury cannot be precipitated by bases. Allocinnamic acid, however, reacts readily giving an anhydride in which the mercury is so attached that it is not precipitated by bases.[50]

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[45] D. R. P. 247,625. *Chem. Zentr.* 1912 II 166.

[46] D. R. P. 281,009. *Chem. Zentr.* 1915 I 73. Fränkel, 670.

[46a] Private communication, G. W. Raiziss.

[47] D. R. P. 234,054. Fränkel, 665. D. R. P. 234,914. *Chem. Zentr.* 1911 II 112. *Chem. Abst.* 6 (1912), 2674. D. R. P. 286,977. *Chem. Abst.* 10 (1916), 1694. Bechhold, *Chem. Zentr.* 1915 I 562.

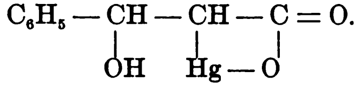
[47a] Private communication, M. S. Kharasch.

[48] D. R. P. 249,332. *Chem. Zentr.* 1912 II 465. *Chem. Abst.* 6 (1912), 2674.

[49] *Ibid.*

[50] Biilmann, *Ber.* 35 (1902), 2576; 43 (1910), 574.

Anhydride of α-hydroxymercuri-β-hydroxyhydrocinnamic acid,[61]



$$\begin{array}{ccccccc} C_6H_5 & - & CH & - & CH & - & C=O. \\ & & | & & | & & | \\ & & OH & & Hg & - & O \end{array}$$

It is prepared by treating allocinnamic acid at 100° with a hot solution of mercuric acetate, formed from mercuric oxide and dilute acetic acid. White microscopic crystals. Yield 2.3 gm. from 1 gm. of the acid.

It is neutral. It is soluble in bases, soluble in carbonates only on heating. Ammonium hydroxide hardly attacks it. No reaction is obtained at first with alkaline sulfide solution, black mercuric sulfide on standing. Potassium iodide gives a clear alkaline solution. It is only slightly soluble in organic solvents. The anhydride can be dissolved in alkali and reprecipitated by carbon dioxide. The reprecipitated substance, however, has a considerably larger per cent of mercury and a smaller per cent of carbon. If the anhydride is dissolved in normal sodium hydroxide and the solution is saturated with hydrogen sulfide and ammonium sulfate is added to completely precipitate the mercuric sulfide a solution is obtained from which an 80 per cent yield of phenyl hydracrylic acid can be extracted. M.P. 91° (Lit. 93°). (Carbon and hydrogen analyses for $C_9H_{10}O_3$.) Boiling the hydracrylic acid with dilute acid gives *common cinnamic acid,* M.P. 133°. If the anhydride is heated with hydrochloric acid it is easily changed to mercuric chloride and common cinnamic acid. The primary product of the splitting by acid must be phenyl hydracrylic acid because allocinnamic acid is not changed to common cinnamic acid by boiling with HCl or with HCl and mercuric chloride. This plausible proof that the splitting of the C — Hg bond by acid precedes any action of the — OH group is of importance in the theories about mercuration of double bond compounds. The fact that the salts of the so-called α-hydroxymercuri-β-hydroxy ethane react with acids giving ethylene has been explained by assuming that the hydroxyl group on the carbon alpha to the C — Hg linkage is unusually reactive and is replaced by chlorine when treated with HCl, even dilute. This would give a compound, $Cl-CH_2-CH_2-HgCl$, which is apparently incapable of existence and therefore loses $HgCl_2$ leaving ethylene. If, as the work with the mercurated cinnamic acid indicates, the C — Hg is first attacked this explanation is weakened and the idea

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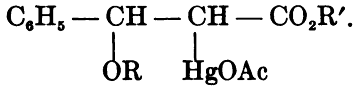
[61] Billmann, loc. cit. 2571 and 575.

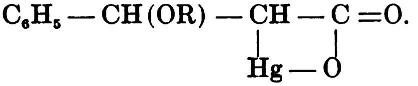
that the ethylene mercuric compounds are not true "structure" compounds is strengthened.

Compounds derived from the mercuration of cinnamic esters in alcohol solution.[52]

Cinnamic esters react with mercuric acetate in alcohol solution in such a way that the groups —HgOAc and —OR are added to the unsaturated carbon atoms respectively, forming compounds,



$$C_6H_5-\underset{OR}{CH}-\underset{HgOAc}{CH}-CO_2R'.$$

The reaction has been carried out in the following alcohols, methyl, ethyl, n-propyl, i-propyl, and i-butyl. The reaction in n-butyl alcohol and in higher and in poly alcohols gives no satisfactory results. When these esters are saponified and then acidified the anhydrides of the corresponding α-hydroxymercuri-β-alkoxy hydrocinnamic acids are obtained,  $C_6H_5-CH(OR)-\underset{Hg-O}{CH-C}=O$. When these anhydrides are dissolved in bases and treated with hydrogen sulfide the C—Hg bond is broken and the corresponding β-alkoxy hydrocinnamic acids are obtained, $C_6H_5-CH(OR)-CH_2-CO_2H$.

Mercuration in methyl alcohol.

α-Acetoxymercuri-β-methoxy hydrocinnamic methyl ester.[53]

Dry mercuric acetate is dissolved in warm methyl alcohol and mixed with one mole of methyl cinnamate. Crystals appear in four hours and the reaction is complete in six, (NaOH test). After standing two days a 65 per cent yield of crystals separates. The rest of the mercurated product may be obtained by evaporation or by treating the mother liquids with sodium chloride solution. The product is dissolved in ethyl acetate and precipitated by adding low boiling ligroin. M.P. 139° (corr. 140.5°) (CHHg). It is easily soluble even in the cold in alcohol, ethyl acetate, acetone and most organic solvents. It forms small needles from ethyl acetate and ligroin, which on standing several days grow to blunt transparent prisms a centimeter long

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[52] Schoeller, Schrauth, and Struensee, *Ber.* 43 (1910), 695; 44 (1911), 1432; 44 (1911), 1048. D. R. P. 228,877. Fränkel, 666.

[53] Schoeller, Schrauth, and Struensee, *Ber.* 43 (1910), 695.

and several millimeters thick. When the ester is heated with slightly over two equivalents of normal base it dissolves. Addition of one equivalent of normal acid causes a white flocculent precipitate of the anhydride. The ester dissolved in warm alcohol and treated with ammonia gas and then with hydrogen sulfide gives mercuric sulfide. The filtrate gives an oil which distills at 248° (corr. 253°) and gives carbon and hydrogen analyses corresponding to β-methoxy hydrocinnamic methyl ester.

Halidemercuri β-methoxy hydrocinnamic methyl esters.[54]

The *chloride* is prepared from the acetate. It crystallizes from ethyl acetate in short needles. M.P. 132.5° (corr. 133.5°) (ClHgCH).

Bromide. Needle crystals. M.P. 110.5° (BrHg). *Iodide.* Needles. M.P. 100° (IHg).

A veronal compound is obtained by treating the acetate with sodium diethyl barbiturate. (NHg).

α-Actoxymercuri-β-methoxy hydrocinnamic ethyl ester.[55]

This compound is prepared from ethyl cinnamate in methyl alcohol and a concentrated aqueous solution of one mole of mercuric acetate. In this case the solution is much less rapid. The sodium hydroxide test does not fail until the mixture has stood for 24 hours (6 in case of the methyl ester). Crystals do not begin to form for three days and the mixture is not filtered for twelve. This difference in the velocities of the reaction may be due to a difference between the reactivity of the two esters or to the fact that water was used in one case and not in the other or to both of these facts. Yield 45 per cent. The product crystallizes from ethyl acetate in small transparent prisms. Very soluble in organic solvents. M.P. 107° (Hg).

(γ-Chloromercuri-β-methoxypropyl) α-chloromercuri-β-methoxyhydrocinnamate,[56]

$C_6H_5-CH(OMe)-CH(HgCl)-CO_2CH_2-CH(OMe)-CH_2HgCl.$

Allyl cinnamate is treated with two moles of mercuric acetate in absolute methyl alcohol. The reaction is complete in a few hours. No crystals separate even on long standing. The solution is treated with sodium chloride solution. An oily precipitate settles which finally

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[54] *Ibid.* 697.

[55] Schoeller, Schrauth, and Struensee, *Ber.* 44 (1911), 1054.

[56] Schrauth and Schoeller, *Ber.* 44 (1911), 1055.

changes to white crystals. These are recrystallized from hot absolute alcohol. White needles. M.P. 169°, gas. It is easily soluble in alcohol, chloroform, benzene, ethyl acetate, easily soluble in sodium hydroxide. Sulfuric acid gives a white flocculent precipitate. (ClHg).

α-Acetoxymercuri-β-methoxy hydrocinnamic benzyl ester.[57]

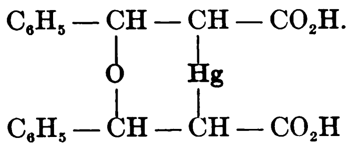
Benzyl cinnamate treated with methyl alcohol and mercuric acetate gives a 50 per cent yield of crystals on standing a few days. Crystallizes from ethyl acetate in colorless silky needles. M.P. 127° (Hg).

Anhydride of α-hydroxymercuri-β-methoxy hydrocinnamic acid.[58]

The corresponding methyl ester is heated with slightly more than two equivalents of normal sodium hydroxide until dissolved and then neutralized with normal sulfuric acid. A white flocculent precipitate is formed. This is pure. It can be dissolved in ethyl acetate and precipitated by adding low boiling ligroin. (CHHg). It decomposes about 184° (corr. 187°). The solution in ammonium hydroxide gives mercuric sulfide at once with ammonium sulfide. Its solution in alkalies gives precipitates with solutions of heavy metal salts.

Methoxy hydrocinnamic acid may be obtained from the mercury compound. The hydroxide is dissolved in normal sodium hydroxide solution and saturated with hydrogen sulfide. Then an excess of solid ammonium sulfate is added to insure the complete precipitation of the mercuric sulfide. The filtrate is barely acidified with normal sulfuric acid and treated with a stream of air to remove all hydrogen sulfide. A white crystalline precipitate is formed. The mixture is extracted repeatedly with ether. The ether is evaporated and the residue is crystallized from hot ligroin. Thick transparent colorless plates separate in 84 per cent yield. The product gives carbon and hydrogen analyses for β-methoxy hydrocinnamic acid.

α-Mercuri-di-β-phenyl-anhydrohydracrylic acid,



$$\begin{array}{ccccccc} C_6H_5 & - & CH & - & CH & - & CO_2H. \\ & & | & & | & & \\ & & O & & Hg & & \\ & & | & & | & & \\ C_6H_5 & - & CH & - & CH & - & CO_2H \end{array}$$

The anhydride of α-hydroxymercuri-β-methoxy hydrocinnamic acid treated with alcohol and an aqueous solution of potassium iodide

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[57] *Ibid.* 1055.

[58] Schoeller, Schrauth, and Struensee, *Ber.* 43 (1910), 697.

gives a solution from which normal sulfuric acid precipitates a white flocculent compound contaminated by a little mercuric iodide. The latter is removed by washing with potassium iodide solution. The yield is ten per cent of the weight of anhydride used. The substance can be recrystallized from alcohol in which it is slightly soluble. It forms white shining rhombic leaflets. It melts and decomposes at 200°. It is practically insoluble in organic solvents but easily soluble in alkalies. It neutralizes two equivalents of sodium hydroxide with phenolphthalein as indicator. (CHHg). The solution in ammonium hydroxide treated with ammonium sulfide gives no mercuric sulfide even on long boiling. Long boiling with concentrated hydrochloric or nitric acid gives mercuric ions. The other product is not mentioned.

Mercuration in Ethyl Alcohol.[59]

α-Acetoxymercuri-β-ethoxy hydrocinnamic methyl ester.

Methyl cinnamate reacts slowly with mercury acetate in ethyl alcohol (better not absolute). After several days a 30 per cent yield of crystals is obtained. More material can be obtained from the mother liquor by adding sodium chloride. It is very soluble in organic solvents. It is best recrystallized from ethyl acetate. M.P. 122.5° (corr. 123°) (CHHg). When the ester is treated with alcoholic ammonia and hydrogen sulfide the C — Hg bond is broken and β-ethoxy hydrocinnamic methyl ester is obtained as a liquid boiling at 251° (corr. 256°). Yield 75 per cent. (CH). Treated with sodium hydroxide and sulfuric acid it forms the anhydride of α-hydroxymercuri-β-ethoxy hydrocinnamic acid.

α-Halidemercuri-β-ethoxy hydrocinnamic methyl esters.

The *Chloride* is prepared from the acetate in the usual way and crystallizes from ethyl acetate in fine needles. M.P. 114° (Hg).

Bromide. Small white needles. M.P. 85° (Hg).

The *iodide* is hard to crystallize. M.P. 71°. It is discolored on standing. (No analysis.)

Anhydride of α-hydroxymercuri-β-ethoxy hydrocinnamic acid.

It is prepared in the usual way from the acetate. It decomposes at about 188° (corr. 191°) with evolution of gas. (CHHg). When treated with sodium hydroxide and hydrogen sulfide, it gives β-ethoxy hydrocinnamic acid in 96 per cent yield. (CH).

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[59] Schoeller, Schrauth, and Struensee, loc. cit. 698 and 1434.

When this acid is boiled a short time with hydrochloric acid it gives common cinnamic acid (M.P. 133°) and ethyl alcohol which is identified by the iodoform test.

Mercuration in n-Propyl Alcohol.

α-Acetoxymercuri-β-n-propoxy hydrocinnamic methyl ester.

The reaction of methyl cinnamate with mercuric acetate in n-propyl alcohol containing a few drops of acetic acid is complete only after several days. In two weeks a 71 per cent yield of crystals forms. These are recrystallized from ethyl acetate. Felted needles. M.P. 134.5° (corr. 135.5°). It is very soluble in organic solvents. (CHHg). The corresponding halides are easily obtained by double decomposition. All are purified by dissolving in ethyl acetate and adding ligroin. *Chloride* M.P. 109° (Hg), *Bromide* M.P. 84° (Hg), *Iodide* M.P. 84° (Hg). The *anhydride* is prepared in the usual way. It decomposes about 185° (corr. 188°) (CHHg). The anhydride yields β-n-propoxy hydrocinnamic acid melting at 59° (CH).

Mercuration in i-Propyl Alcohol.

α-Acetoxymercuri-β-i-propoxy hydrocinnamic methyl ester.

The reaction runs about the same as in normal propyl alcohol. Solution in ethyl acetate leaves some mercurous acetate undissolved. M.P. 148° (corr. 150°) (CHHg). The halides have been made but not studied. The *anhydride* is made as usual. Yield 87 per cent. It decomposes about 188° (corr. 191°) (CHHg). When the anhydride is decomposed in alkaline solution by sulfides it gives a 53 per cent yield of β-i-propoxy hydrocinnamic acid, M.P. 73° (CH).

Mercuration in Isobutyl Alcohol.

α-Acetoxymercuri-β-i-butoxy hydrocinnamic methyl ester.

Methyl cinnamate dissolved in isobutyl alcohol is treated with a concentrated solution of mercuric acetate in warm water containing a few drops of acetic acid to prevent the formation of mercuric oxide. The reaction is complete in 8 days. A 35 per cent yield of crystals is obtained in 17 days. Some mercurous acetate is formed. It is purified by ethyl acetate in the usual way. (CHHg). M.P. 152° (corr. 154°). The halides have not been made. The *anhydride* is made in the usual way. Yield 94 per cent. It decomposes about 190° (corr.

193°) (CHHg). The anhydride gives the corresponding β-alkoxy hydrocinnamic acid in 92 per cent yield. M.P. 67.5° (CH).

Phenyl propiolic esters are said to react with mercuric acetate in alcohol solution in the same way as cinnamic esters.

Mercury Derivatives of Salicylic Acids.[60]

When mercuric salicylate is heated to about 100° it changes to the substance known as "basic mercury salicylate" which is really a C — Hg compound or a mixture of such compounds. The chief constituents of the mixture is the anhydride of 3-hydroxymercuri-2-hydroxybenzoic acid. Other constituents are the anhydride of the corresponding 5-hydroxymercuric compound and the anhydride of 3-hydroxymercuri-5-salicylatemercuri-2-hydroxybenzoic acid.

Anhydride of 3-hydroxymercuri-2-hydroxybenzoic acid.

It is prepared by boiling salicylic acid with mercuric oxide. It forms a fine white powder completely soluble in sodium hydroxide, insoluble in water and all organic solvents. The solution in sodium carbonate or sodium hydroxide is precipitated by carbon dioxide. It decomposes on heating. (CHHg). It is soluble in sodium chloride solution forming the sodium salt of chloromercurisalicylic acid. Hydrogen sulfide and ammonium sulfide react only on heating. Treatment with iodine gives o-iodosalicylic acid. Dilute acid splits inorganic mercury from the anhydride. When solid mercuric salicylate is heated above 100° it forms salicylic acid and the C — Hg anhydride. The free acid can be washed out with alcohol and ether. The change to the C — Hg compound takes place more easily than in the unsubstituted benzoic acid. Mercuric benzoate must be heated to 170° to cause the mercury to replace hydrogen of the nucleus.

3-Halidemercuri-2-hydroxy benzoic acids.[61]

These are obtained by treating the anhydride with alkali halides and adding dilute acetic acid to precipitate the free acid from the solution of the alkali salt first formed. They are obtained as gelatinous precipitates which become crystalline on standing. They are slightly

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[60] Buroni, *Gazz. chim. ital.* 32 II (1902), 305. *Chem. Zentr.* 1903 I 578. Dimroth, *Ber.* 35 (1902), 2033, 2873. Brieger, *Arch. Pharm.* 250 (1912), 62. *Chem. Zentr.* 1912 I 753. Gadamer, *Arch. Pharm.* 256 (1919), 263. *Chem. Abst.* 13 (1919), 1364.

[61] Buroni, loc. cit. 310.

soluble in alcohol. Metallic salts of the hydroxymercuri salicylic acid are obtained by dissolving the anhydride in aqueous or alcoholic alkali and evaporating the solution to crystallization in a vacuum.

3, 3′-Mercuribis-2-hydroxy benzoic acid.[62]

It is prepared by a neutral reduction of the anhydride. The heavy white powder is insoluble in water. It is decomposed by heat. It gives soluble neutral alkali salts.

Mercury acetyl salicylate.[63]

When the mercuric salt of acetylsalicylic acid is heated for some time at about 100° it changes to a glassy mass which does not give mercury reactions with sodium hydroxide or ammonium sulfide.

Acetoxymercuri salicylic methyl ester.[64]

It is prepared by heating mercuric acetate with methyl salicylate and a small amount of acetic acid for 40 minutes. Crystals separate on cooling. Yield 52 per cent. It is dissolved in hot ethyl acetate and precipitated by adding low boiling ligroin. (CHHg). M.P. 202° (corr.), after slight sintering. It dissolves easily in warm methyl and ethyl alcohols, in ethyl acetate, acetone, and chloroform. It is difficultly soluble in water. Alkalies dissolve it with saponification of the ester. It is fairly stable to ammonium sulfide but less so than the corresponding mercurated benzoic ester. It is easily decomposed by halogen acids.

Chloromercuri salicylic methyl ester.

The mother liquor from the acetate is treated with sodium chloride. It is purified by dissolving in ethyl acetate and adding low boiling ligroin. (CHHgCl). It is less soluble in alcohol and other organic solvents than the acetate. It is fairly stable to ammonium sulfide but less so than the benzoic compound.

Sulfidemercuri salicylic methyl ester.

It is prepared from a cold methyl alcohol solution of the acetate treated with the calculated amount of an alcoholic solution of hydrogen sulfide. The amorphous white precipitate is filtered off. Yield 85 per cent. If allowed to stand in the mother liquor it turns yellow.

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[62] D. R. P. 255,030. *Chem. Zentr.* 1913 I 248.

[63] Gerngross and Kersasp, *Ann.* 406 (1914), 248.

[64] Schoeller and Schrauth, *Ber.* 53 (1920), 639.

(S Hg). It is soluble in chloroform, benzene, and aniline, soluble in dilute alkalies and alkali sulfides. It has no definite melting point. When the sulphide is warmed for a short time with dilute nitric acid a precipitate of mercuric sulfide is formed. This contains all of the sulphur and half of the mercury in the original sulfide.

Mercuribis-salicylic methyl ester.

The sulfide is heated at 110° for 6 hours. The black residue is powdered and extracted with ethyl acetate giving a 12 per cent yield of the R_2Hg compound. It is better prepared by the action of sodium thiosulfate on the acetate. (CHHg). It is easily soluble in methyl and ethyl alcohol, acetone, ethyl acetate, chloroform, and benzene. Difficultly soluble in ether and low boiling ligroin. M.P. 178-80°.

Acetoxymercuri salicylic ethyl ester.[65]

Ethyl salicylate is heated to 180° in a glycerine bath and treated with finely powdered mercuric acetate in small portions. The amorphous brown product dissolves on further heating. When no mercuric ions are present the solution is cooled. An almost quantitative yield of crystals is obtained. It recrystallizes from ligroin and ethyl acetate. (CHHg). It sinters at 200° and melts at 206° (corr.). Its solubilities are like those of the methyl ester.

Mercuribis-salicylic ethyl ester.

The acetate is powdered and dissolved in cold saturated sodium thiosulfate. An amorphous precipitate separates almost immediately. The mother liquor gives an amount of mercuric sulfide with ammonium sulfide corresponding to almost exactly one-half of the mercury in the original compound. Yield 82 per cent. The impure substance is dried in a vacuum and extracted with acetone and recrystallized from ether. (CHHg). Its solubilities are like those of the methyl ester. M.P. 193° (corr.).

Water soluble compounds of mercuri salicylic anhydride.[66]

The insoluble anhydride unites with a great variety of organic substances forming water soluble compounds. Among the substances

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[65] *Ibid.* 641.

[66] Buchtala. *Z. physiol. Chem.* 83 (1913), 280, 283. Schoeller and Schrauth. *Therap. Monatsch.* 23 (1909), 4. *Chem. Zentr.* 1910 I 948. *Chem. Zentr.* 1910 II 609. *Chem. Abst.* 5 (1911), 156; Ger. Pat. 224,435. *Chem. Zentr.* 1910 II 701; Ger. Pat. 224,864. *Chem. Zentr.* 1910 II 1423. *Chem. Abst.* 5 (1911), 2154; Ger. Pat. 227,391. Engelmann, *Chem. Abst.* 5 (1911), 971; U. S. Pat. 978,145. Bayer & Co., *Chem. Abst.* 5

which form these compounds are sodium β-amino-α-oxyisobutyrate, sodium diethyl barbiturate, sodium-α-amino isobutyrate, piperazine, various acid imides, parabanic acid, acid ureides in general, urea, dicyandiamide, urethanes, nucleic acids, albumens, xanthine bases, and mercury compounds of sulfamidobenzoic acids containing the group, $-SO_2-NH-HgOH$.

3-Acetoxymercuri-5-nitro-salicylic acid is obtained from 5-nitrosalicylic acid and mercuric acetate in water solution.[66a] The corresponding *chloride* is obtained by boiling 5-nitrosalicylic acid with fresh mercuric oxide, dissolving the product in alkali, and precipitating the solution with dilute hydrochloric acid. (NHg).[66a]

3, 5-Dinitrosalicylic acid reacts with a boiling water solution of mercuric acetate giving an organic mercury compound the structure of which has not been determined.[66a] The *chloride* has been made. (NClHg).

5-Aminosalicylic acid reacts with mercuric acetate in water solution giving an *acetoxymercuri compound*. The position of the mercury is not known.[66a] The corresponding *chloride* has been prepared.

5-Acetaminosalicylic acid when heated with fresh mercuric oxide gives a *hydroxymercuri compound*. (NHg).[66a] Its structure is not known. The *chloride* has been prepared.

3-Bromo-5-nitro-salicylic acid gives an *acetoxymercuri compound* of unknown structure, when heated with mercuric acetate in water solution.[66a]

2-Mercuri-5-hydroxy-benzoic acid compounds.[67]

The anhydride is prepared by boiling the mercuric salt of m-hydroxy benzoic acid. The anhydride gives water soluble compounds when treated with acetamide, and a great variety of organic nitrogen compounds. Most important of these are veronal (barbital) and alpha amino acids.

(1911), 3880; U. S. Pat. 1,001,829. Schoeller and Schrauth, *Biochem. Z.* 33 (1911), 381. *Chem. Zentr.* 1911 II 707. *Chem. Zentr.* 1911 I 275-6; Ger. Pats. 229,574, 229,575, 229,781. Buchtala, *Z. physiol. Chem.* 83 (1913), 249. Blumenthal. *Biochem. Z.* 57 (1913), 261. *Chem. Zentr.* 1914 I 137. Schmidt. *Pharm. Z.* 60 (1916), 724; *Chem. Abst.* 10 (1916), 951. D. R. P. 224,864. *Chem. Zentr.* 1910 II 701. D. R. P. 247,625. Fränkel, 668. Schmidt, *Pharmazeutische Chem.* II 1180. Fränkel, 662.

[66a] Private communication, G. W. Raiziss.

[67] D. R. P. 229,575. *Chem. Zentr.* 1911 I 276. D. R. P. 229,781. *Ibid.* Engelmann, *Chem. Abst.* 7 (1913), 2094. Lajoux, *Chem. Abst.* 9 (1915), 2527.

2-Mercuri-4-hydroxy-benzoic acid compounds.[68]

When the mercuric salt of p-hydroxy benzoic acid is heated complex basic salts are said to be obtained. The product probably contains C — Hg compounds.

2, 2'-Mercuribis-4-hydroxy-benzoic acid.[69]

The corresponding amino compound is diazotized, boiled with water, dissolved in sodium hydroxide and precipitated by acetic acid.

3-Hydroxymercuri-2-hydroxy-5-sulfobenzoic acid.[70]

It is prepared in the usual way from the acid heated with mercuric compounds. It is soluble in water but insoluble in organic solvents. Ammonium sulfide gives a dark color but no precipitate. Alkaline or neutral reduction gives the R_2Hg compound, *3-Mercuribis-2-hydroxy-5-sulfobenzoic acid.*

3-Hydroxymercuri-4-hydroxy-5-carboxyl phenyl arsonic acid.[71]

It is prepared in the same way as the corresponding sulfonic acid. Alkaline or neutral reduction gives the R_2Hg compound.

Mercury Derivatives of Methoxybenzoic Acids.

Anhydride of 3-hydroxymercuri-6-methoxybenzoic acid.[72]

It is prepared by heating a paste of o-methoxybenzoic acid and mercuric acetate and water on the steam bath. It is soluble in chloroform, insoluble in sodium hydroxide. This insolubility is unusual.

Anhydride of 3-hydroxymercuri-4-methoxybenzoic acid.[73]

The mercury salt of anisic acid does not give a "basic" salt when boiled with water. It changes only on heating to about 140°. The mercury probably takes the position meta to the carboxyl group.

Sodium salt of 2-hydroxymercuri-4-methoxybenzoic acid.[74]

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[68] Blumenthal and Oppenheim, *Biochem. Z.* 39 (1912), 51. *Chem. Abst.* 6 (1912), 1467.

[69] *Ibid.*

[70] Schoeller, Schrauth, and Müller, *Biochem. Z.* 33 (1911), 399. D. R. P. 216,267. D. R. P. 255,030. *Chem. Zentr.* 1913 I 353.

[71] D. R. P. 255,030, *ibid.*

[72] Lajoux, loc. cit.

[73] *Ibid.*

[74] D. R. P. 234,054. Fränkel, 665.

Mercury compound of veratric acid, 3, 4-dimethoxybenzoic acid.[75]

Mercury compounds of tyrosine.[76]

Mercury derivatives of di-iodotyrosin.[77]

Isatin mercury compounds.[78]

Mercury derivatives of hydroxynaphthoic acids.[79]

Phthalic acid reacts with mercuric acetate on refluxing and loses carbon dioxide forming the anhydride of o-hydroxymercuribenzoic acid.[80]

Mercury phthalimide. N — Hg compound.[81]

Mercury Derivatives of Phenolphthalein and Related Compounds.[82]

A great variety of compounds of this type have been mercurated. Among these are phenolphthalein, fluorescein, methyl fluorescein, dibromfluorescein, tetrabromfluorescein, tetraiodofluorescein, tetraiodophenolphthalein, quinolphthalein, resorcin succinein, cresorcin succinein, resorcin saccharein. In several cases the compounds have been carefully studied and the results are available in the literature.[83]

In some cases mercuration is carried out by heating the sodium salt with mercuric oxide. By this method 3 mercury atoms can be introduced into phenolsulfonephthalein, two into fluorescein, and one, with difficulty, into phenolphthalein. This method will not serve to introduce mercury into the di- or tetra halogen fluoresceins. If mercuric acetate is used in alcohol or water solution or suspension all of the positions ortho to phenolic oxygen are replaced by mercury except in the case of phenolphthalein into which only three atoms of mercury can be introduced instead of the expected four.

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[75] D. R. P. 249,332. *Chem. Zentr.* 1912 II 465. Fränkel, 665.

[76] R. Hofmann, *Ann.* 87 (1853), 124. D. R. P. 279,957. *Chem. Zentr.* 1914 II 1334. Buchtala, *Chem. Abst.* 12 (1918), 1909; 10 (1916), 805, 1578, 1693. D. R. P. 279,957. Fränkel, 661.

[77] D. R. P. 279,957, loc. cit.

[78] Peters, *Ber.* 40 (1907), 235.

[79] Brieger and Schulemann, *J. prakt. Chem.* (2) 89 (1914), 176.

[80] Pesci, *Gazz. chim. ital.* 32 II (1902), 279.

[81] Landsberg, *Ann.* 215 (1882), 189.

[82] White, *J. Am. Chem. Soc.* 42 (1920), 2355. D. R. P. 308,335. *Chem. Abst.* 13 (1919), 1621.

[83] *Ibid.*

Tri-acetoxymercuri phenolphthalein.[84]

Phenolphthalein and mercuric acetate are heated in dilute alcohol and acetic acid. Rosetted needles. (Hg,HOAc). At 120° it loses one molecule of acetic acid, probably forming an anhydride of an o-hydroxymercuri phenol.

Hydroxymercuri phenolphthalein.[85]

It is prepared by boiling a solution of phenolphthalein in dilute sodium hydroxide with mercuric oxide for three hours. The alkaline solution is filtered to remove a black residue and precipitated by carbon dioxide as a purplish white amorphous solid. (Hg). It is insoluble in common solvents except acetic acid.

Di-acetoxymercuri-o-cresolphthalein.[86]

The preparation in water solution forms considerable amounts of mercurous acetate. The product is a yellow granular substance (Hg). It is insoluble in common solvents but soluble in bases giving a purple solution.

Tri-hydroxymercuri phenolsulfonephthalein.[87]

An alkaline solution of the phthalein is boiled with mercuric oxide for several hours. The purple solution is cleared by means of the centrifuge and evaporated on a steam bath. It leaves a purple powder with a bronze luster. (Hg).

Tetra-acetoxymercuri phenolsulfonephthalein.[88]

This substance could not be obtained pure by boiling the phthalein with mercuric acetate. Instead a substance is obtained which gives analyses indicating that it is a mixture of one molecule of this substance with two molecules of its hydrolysis product, ***tetra-hydroxy-*** *mercuri phenolsulfonephthalein.* The hydrolysis cannot be made complete. The product is insoluble in all solvents except methyl alcohol, hot acetic acid, and sodium hydroxide. In the latter it gives a bluish purple solution.

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[84] White, loc. cit. 2362.
[85] *Ibid.* 2360.
[86] *Ibid.*
[87] *Ibid.*
[88] *Ibid.* 2365.

Tetra-acetoxymercuri fluorescein.[89]

As is the case of the preceding compound this substance is not obtained pure but in a partly hydrolyzed condition. The product from fluorescein, sodium hydroxide and mercuric oxide is about two-thirds hydroxide and one-third acetate. It is insoluble in common solvents but soluble in bases. An alkaline solution of iodine gives the color of erythryrosin.

Hydroxymercuri fluorescein.[90]

Prepared from an alkaline solution of fluorescein and one molecule of mercuric oxide. Treated with dilute HCl it gives a *chloromercuri compound.* (Cl). With sulfuric acid it gives the *hydroxymercuri* compound.

Di-hydroxymercuri fluorescein.

It is prepared like the preceding compound but by the use of two molecules of mercuric oxide. It forms iridescent green scales. (Hg).

Hydroxymercuri-dibromo-fluorescein.[91]

Prepared from an alkaline solution of dibromofluorescein boiled with mercuric acetate and acetic acid until a sample gives no action with ammonium sulfide. (Hg). Less than one per cent of acetic acid is obtained from the substance showing that the change to the hydroxymercuri compound is almost complete. The product is a red powder, insoluble in common solvents, soluble in two molecules of sodium hydroxide giving a deep red solution. It is soluble in ammonium sulfide. Mercuric sulfide separates slowly from this solution.

Mercury *vanillin* is a white tasteless solid, soluble in water, soluble in dilute acids. It is a sweet smelling powder containing 40 per cent of mercury.[92]

[89] White, *J. Am. Chem. Soc.* 42 (1920), 2363.
[90] *Ibid.* 2360.
[91] *Ibid.* 2363.
[92] *Realenzyk. Pharm.* VII 100.

Chapter XIII.

Mercury Derivatives of Aromatic Ketones, Terpenes, and Related Compounds.

Derivatives of Acetophenone.

Phenacyl mercuric chloride, $C_6H_5 — CO — CH_2 — HgCl$.[1]

Mercuric acetate is heated with an excess of acetophenone at 150° until no mercuric ions can be detected by sodium hydroxide. The clear solution is filtered from the mercury which is formed, into a sodium chloride solution. The precipitate is washed with small portions of ether to remove any unchanged acetophenone. It is recrystallized from high boiling ligroin or acetone. M.P. 145-6° (C, high, HHg). The mercury is very loosely attached. Warm dilute hydrochloric acid gives acetophenone. Even cold dilute ammonium sulfide gives HgS at once. Bromine dissolved in potassium bromide gives phenacyl bromide which is identified by its melting point, analysis, and the formation of the aniline compound melting at 94°. The mercuration of acetophenone gives a small amount of dimercurated product.

Phenacyl mercuric chloride reacts with ethyl magnesium bromide in an atmosphere of hydrogen giving the tertiary alcohol *(Chloromercuri methyl)-ethyl-phenyl-carbinol.* M.P. 129-30° decomp. It is a yellow solid which can be recrystallized from ether. (CHHg). It gives mercuric sulfide at once with ammonium sulfide.

Acetophenone is said to react with alkaline mercuric iodide.[2] It reacts with mercuric oxide if heated for a long time at 100°. The resulting product is a pale yellow insoluble compound which reacts with hydrochloric acid giving acetophenone.[3]

It reacts with alkaline mercuric cyanide solution giving a light

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[1] Dimroth, *Ber.* 35 (1902), 2870. Grignard and Abelmann, *Bull. soc. chim.* (4) 19 (1916), 19.

[2] Marsh and Fleming-Struthers, *J. Chem. Soc.* 95 (1909), 1778.

[3] Hantzsch and Auld, *Ber.* 38 (1905), 2683.

yellow precipitate which gives analyses for C, H, N, Hg, and CN which agree very well with the formula, $C_{24}H_{18}O_3Hg_4(CN)_2$.[4]

Mercury Derivatives of Benzophenone.[5]

Alkaline mercuric iodide or mercuric oxide give no action on benzophenone which thus differs from ketones which are capable of forming an enol modification. Mercuric acetate reacts with benzophenone at 150° giving an ortho mercurated product.

o-Chloromercuri benzophenone.[6]

Dry mercuric acetate is heated with three molecules of benzophenone in a bulb at 150° until the reaction is complete. The warm mixture is poured into sodium chloride solution and then cooled and shaken with ether. Evaporation of the ether leaves benzophenone and the mono compound and a small amount of a dimercurated product of unproved structure. The benzophenone is removed by hot ligroin. The residue is repeatedly crystallized from alcohol. Shining leaflets. M.P. 167-8°. It is easily soluble in acetone, chloroform, and ethyl acetate, very difficultly soluble in ligroin. Yield 40° of weight of mercuric acetate used. (CHHg). Boiling hydrochloric acid splits the C — Hg linkage. Hydrogen sulfide acts very slowly even on heating. Ethyl magnesium bromide forms a mercurated tertiary alcohol.

Phenyl o-chloromercuriphenyl ethyl carbinol.

Is prepared in the same way as the corresponding compound from phenacyl mercuric chloride. It is recrystallized from a mixture of ether and ligroin. M.P. 106° decomp. (CHHg). It reacts vigorously with Grignard reagents. It gives no action in the cold with ammonium sulfide or hydrogen sulfide.

o-Bromomercuri benzophenone.

It is prepared from the mercuration mixture and sodium bromide. It is less soluble in ether and alcohol than the chloride. M.P. 176° (CHHgBr). Treatment with bromine yields o-bromobenzophenone. This substance is identified by its melting point, its oxime, and the *phenyl indoxazene* obtained from the latter.

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[4] Marsh and Fleming-Struthers, *J. Chem. Soc.* 87 (1905), 1881.

[5] Dimroth, *Ber.* 35 (1902), 2868. Auld and Hantzsch, *Ber.* 38 (1905), 2677. Marsh and Fleming-Struthers, *J. Chem. Soc.* 95 (1909), 1778. Grignard and Abelmann, *Bull. soc. chim.* (4) 19 (1916), 20.

[6] Dimroth, loc. cit. Grignard and Abelmann, loc. cit. 24.

2-Chloromercuri indandione.[7]

The sodium derivative of indandione is treated with an excess of mercuric chloride. (ClHg). The product is a yellow solid easily soluble in pyridine, difficultly soluble in sodium hydroxide. Cold sodium carbonate solution changes it to the corresponding hydroxide.

2-Hydroxymercuri indandione.[8]

Is prepared from the chloride by shaking two days with sodium carbonate solution. The residue is washed with dilute acetic acid to remove any mercuric oxide. White solid. (Hg).

2-chloromercuri-2-acetyl-indandione.[9]

Is prepared from the sodium salt and mercuric chloride. White microcrystalline powder.

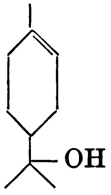
2-Chloromercuri-2-carbethoxy-indandione.

The sodium compound and mercuric chloride on standing several days give colorless cubes. M.P. 240-5° (ClHg). Insoluble in common solvents, soluble in pyridine with yellow color. When the pyridine solution is treated with water a precipitate of $HgCl_2.2C_5H_5N$ is formed. The other product is not mentioned.

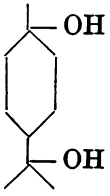
2, 2'-Mercuribis-2-carbethoxy indandione.[10]

It is prepared from the sodium compound and mercuric acetate. (Hg).

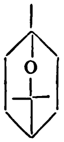
Mercury Compounds Formed from Terpineol.[10a]



Terpineol.



Terpinol.
(Terpine).



Cineol.

Terpineol does not give any satisfactory product with acid solutions of mercuric salts. Mercuric oxide is dissolved in 20 per cent nit-

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[7] Peters, *Ber.* 40 (1907), 239.

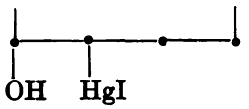
[8] *Ibid.*

[9] Hantzsch and Gajewski, *Ann.* 392 (1912), 309.

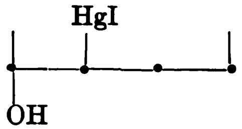
[10] *Ibid.* 307.

[10a] Sand and Singer, *Ber.* 35 (1902), 3171.

ric acid and the solution is treated with 10 per cent potassium hydroxide until the white basic salt begins to form. A solution of terpineol in ether is added and shaken until the precipitate dissolves. Potassium hydroxide is added until the basic salt is again precipitated. This is dissolved by the addition of more terpineol solution. These processes are kept up until addition of potassium hydroxide gives a black precipitate. The water layer is then separated and filtered. The amount of mercury in the solution is carefully determined by analyzing an aliquot part. The solution is made strongly alkaline with concentrated potassium hydroxide and the calculated amount of potassium iodide solution is added in three portions. The alkali insoluble cineol mercuric iodide precipitates at once. In a few days the filtrate gives crystalline crusts of the high melting α-trans-terpinol mercuric iodide. The filtrate from this substance when treated with carbon dioxide gives a precipitate of the low melting β form of trans-terpinol mercuric iodide, the chief product of the reaction. Another product, yellow and amorphous is obtained.



α-Trans-terpinol mercuric iodide.
Stable form.
High melting.



β-Trans-terpinol mercuric iodide.
Labile form.
Low melting.

If the solution is strongly enough alkaline before the addition of potassium iodide the mercury cineol iodide contains some of the β-terpinol iodide. This can be extracted with cold alcohol. This alcoholic extract when treated with water and evaporated under diminished pressure gives some of the α iodide, then a mixture of the α and β and finally an oil which is mainly the β form.

2-Chloromercuri cineol.[11]

Is prepared by adding the calculated amount of potassium chloride to the solution obtained from terpineol and basic mercuric nitrate without the addition of a large excess of alkali. After the mixture has been allowed to stand for 24 hours it is treated with carbon dioxide. The precipitate is recrystallized from alcohol. It forms white

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[11] *Ibid.* 8175.

matted needles. M.P. 162°. It is soluble in alkalies thus differing from the iodide. Otherwise its solubilities are like those of that substance. (CHHg). When reduced with sodium amalgam it gives an oil which may be impure cineol. Treatment with sodium stannite gives mercury dicineolyl.

2-Iodomercuri cineol.[12]

Is prepared as outlined above. 86 gm. of mercuric oxide gives 16 gm. of the iodide. It crystallizes from alcohol in beautiful small prisms. Turns yellow, 115°, melts 152-4° decomp. (CHIHg). It is insoluble in alkalies and potassium iodide solution. It dissolves in concentrated mineral acids with decomposition. It is difficultly soluble in ether and cold alcohol, easily in hot alcohol, very soluble in cold benzene and chloroform. Reduction with sodium amalgam gives an oil which does not crystallize on long standing or when seeded with terpineol crystals. It may be impure cineol. The iodide gives no benzoate when treated with benzoyl chloride and pyridine showing it is not a derivative of terpineol.

2, 2′-Mercuribis-cineol, 2-Mercury dicineolyl.[13]

Is prepared from the chloride and sodium stannite. It is an oil insoluble in alkalies, but easily decomposed by acids giving terpineol. It gives a compound containing oxalic acid when treated with an ether solution of that substance.[14]

α-Form of 2-iodomercuri-trans-terpineol. (Stable, high melting form.)

Preparation as above. It crystallizes from benzene in small colorless crystals which are sensitive to light. It turns red at 120°, melts 144° decomp. (CHIHg). Soluble in strong potassium hydroxide, difficultly soluble in cold benzene and ethyl acetate, easily soluble in alcohol, ether, and hot benzene. It can be obtained by evaporating an ether solution of the labile β-isomer. It forms a fairly *stable compound* with one molecule of alcohol. This is easily soluble in cold absolute alcohol. It separates in shining needles. M.P. 123-5° turning red ($CHHg,C_2H_5OH$). Solution in benzene gives the α-iodide. M.P. 144°. Electrolytic reduction of an alkaline solution of the iodide gives pure trans-terpinol. M.P. 156°. Reduction by sodium amalgam gives an 85 per cent yield of the same substance.

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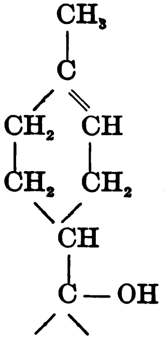
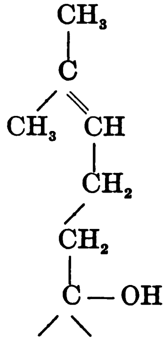
[12] *Ibid.* 3174.
[13] *Ibid.* 3176.
[14] *Ibid.* 3177.

β-*Form of 2-iodomercuri-trans-terpinol.* (Labile, low melting form.) Is prepared by passing carbon dioxide into the cooled liquid from which cineol mercuric iodide and the α-terpinol mercuric iodide have separated. The white precipitate is purified by dissolving in potassium hydroxide and precipitating fractionally by carbon dioxide. M.P. 38°. It separates from benzene solution as a clear oil. (CH). It is very soluble in alcohol, ether, ethyl acetate, rather difficultly in cold benzene, and ligroin, easily soluble in potassium hydroxide or potassium iodide solution. Reduction by sodium amalgam gives trans-terpinol. It is easily soluble in cold acetic acid. When this solution is heated it suddenly gives a mass of white crystals of the α-iodide melting at 144°. About two-thirds of the beta form is changed. On standing in cold alcohol solution the beta iodide slowly gives crystals of the alcohol compound of the alpha iodide, M.P. 123°. Recrystallization of the beta form from benzene gives a mixture of the two isomers. The change from the beta form to the more stable form takes place very slowly in alkaline solution.[15] *Dimethyl heptenol* has a structure much like that of terpineol.


Terpineol.


Dimethyl heptenol.

When treated with mercuric acetate it gives a mercurated inner ether analogous to mercury cineol iodide and a mercurated glycol much like the mercurated trans-terpinol. This glycol appears to have an oily modification analogous to the beta form of the terpinol compound.

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[15] *Ibid.* 3184.

3-Iodomercuri-2, 6-dimethyl-2, 6-epoxyhexane.

Is formed from dimethyl heptenol and mercuric acetate treated with potassium hydroxide after a few seconds. It is an oil, insoluble in concentrated KOH, soluble in absolute alcohol and ether. (CH).

3-Iodomercuri-2, 6-dimethyl-hexandiol, 2, 6.

Is prepared by passing carbon dioxide into the alkaline filtrate from the preparation of the preceding compound. The precipitate is extracted with ether. This on evaporation leaves an oil which solidifies on standing or if warmed with benzene. It crystallizes from benzene. M.P. 124-5° sharp. It is sensitive to light. (CH). It dissolves in potassium hydroxide.

Mercury Derivatives of Camphor.[16]

Camphor reacts with an alkali and mercuric iodide giving complex mercury compounds which are formulated as, $(C_{10}H_{14}O)Hg_2I_2$, $(C_{10}H_{14}O)_3Hg_4I_2$, $(C_{10}H_{14}O)_4Hg_5I_2$, and $(C_{10}H_{14}O)_5Hg_6I_2$. Treatment of these compounds with iodine, iodine chloride, or iodine bromide gives di-iodocamphor which can be changed to camphoquinone. This indicates that the alpha hydrogen atoms of camphor are replaced by mercury.

aa-Di-iodomercuri camphor.[17]

Is prepared from camphor and a cold potassium hydroxide solution and mercuric iodide. It can also be prepared by adding cold acetic acid to the yellow precipitate of $(C_{10}H_{14}O)_3Hg_4I_2$ formed from camphor boiled with an alkaline solution of potassium mercuric iodide.[18]

It forms a colorless amorphous powder, insoluble in water and neutral solvents. It sublimes without decomposition. It is not changed by aqueous potassium iodide. It is insoluble in alcohol and acetone. A mixture with potassium iodide is soluble in alcohol and acetone.

a-Acetoxymercuri camphor.[19]

Is prepared by dissolving $(C_{10}H_{14}O)_3Hg_4I_2$ in hot acetic acid.

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[16] Marsh and Fleming-Struthers, *J. Chem. Soc.* 95 (1909), 1778. Marsh, *J. Chem. Soc.* 97 (1910), 2413.

[17] Marsh and Fleming-Struthers, *J. Chem. Soc.* 95 (1909), 1783.

[18] *Ibid.* 1780.

[19] *Ibid.* 1782.

α-Halidemercuri camphor.

If $(C_{10}H_{14}O)_3Hg_4I_2$ is treated with cold acetic acid and then with a chloride or bromide solution the corresponding halide is obtained. The *chloride* is slightly soluble in dilute acetic acid, giving good crystals. It melts 222° (ClHg).

The *bromide* is insoluble in water, soluble in acetic acid giving colorless crystals which melt at 220-1° (BrHg). The *iodide* is obtained in this way in the form of a double salt with a molecule of mercuric iodide. If an excess of potassium iodide is added in the presence of acetic acid the C — Hg compound is decomposed. If the treatment with an excess of potassium iodide is carried out in a neutral medium the molecule of mercuric iodide is removed leaving the iodomercuri camphor. (CHIHg).

Oxide of α-mercuri camphor.[20]

The acetate solution obtained from $(C_{10}H_{14}O)_3Hg_4I_2$ is treated with an excess of 10 per cent chloride-free sodium hydroxide. The precipitate is readily soluble in alcohol and carbon disulfide. No good crystals are obtained. Heated above 100° it apparently gives a more complicated mercurated camphor. (CHHg). Treated with acids it gives various salts such as the sulfate, nitrate, oxalate, and benzoate.

Camphocarboxylic acid and its esters give stable organic mercury compounds.[21]

Mercury Derivatives of Camphene.[22]

Camphene dissolved in petroleum ether is shaken with a saturated solution of two molecules of mercuric acetate for thirty days. A white resinous substance is formed which gradually hardens. Yield 90 per cent. Slightly soluble in water and alcohol. M.P. 188-9°. Analyses for C, H, and Hg agree with the formula $(C_{10}H_{16}O)\ (HgOAc)_2$. This formula would indicate that one molecule of basic mercuric acetate has added to the molecule and that one acetoxymercuri group has been introduced in place of a hydrogen atom. It reacts slowly with dilute hydrochloric acid and hydrogen sulfide forming camphene. The

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[20] *Ibid.* 1785.

[21] D. R. P. 275,932. *Chem. Zentr.* 1914 II 367. Fränkel, 667.

[22] Balbiano and Paolini, *Atti accad. Lincei* (5) 11 I (1902), 65. *Chem. Zentr.* 1902 II 844. *Ber.* 36 (1903), 3576. *Gazz. chim. ital.* 36 I (1906), 250.

corresponding dichloromercuri compound is prepared from the acetate and sodium chloride. It is an amorphous white powder, insoluble in all neutral solvents. It softens at 150° but does not melt at 250° (ClHg). Treatment with sodium amalgam or with zinc and sodium hydroxide gives an odor of camphene. Heating gives some camphene.

Treatment of *pinene*[23] with mercuric acetate gives mercurous acetate and an oxidation product, Δ^6(6)-hydroxy-menthen-2-one.

Mercury Compounds of Resins and Glucosides.[24]

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[23] *Ibid.*, see also Balbiano and Paolini, *Ber.* 35 (1902), 2995.

[24] Schoeller and Schrauth, *Chem. Abst.* 10 (1916), 395. Leys, *J. pharm. chim.* (6) 21 (1905), 388. *Chem. Zentr.* 1905 I 1532. Schmidt, *Pharmazeutische Chem.* II 2002.

Chapter XIV.

Mercury Derivatives of Heterocyclic Compounds, Azo Compounds, and Aromatic Arsenicals.

Mercury Compounds of Thiophene.

Thiophene reacts with an acid solution of mercuric sulfate giving a series of compounds which are formulated as double salts with mercuric sulfate and mercuric oxide.[1]

α-Chloromercuri thiophene.[2]

Thiophene in alcohol is treated with saturated mercuric chloride solution and a 33% solution of sodium acetate. After several days a white crystalline precipitate is formed. Yield 25 gm. from 10 gm. of thiophene. The mono-mercury compound is separated from the di-mercury compound by extraction with hot alcohol. It is almost insoluble in cold water, slightly soluble in hot. It is recrystallized from hot acetone or chloroform. M.P. 183°. If heated for some time it becomes solid and does not melt again. It is slightly volatile and sublimes even at 100° and very rapidly at 210°. If heated in large amounts it is blackened. ($CHClSHg$). The chloride is soluble in a large volume of 4% sodium hydroxide. It is precipitated unchanged by acetic acid.

Reactions.

1. With halogens.[3]

It does not react with iodine. This is the more peculiar as the 2, 5-dichloromercuri thiophene does react with halogens.

2. With acid halides.

Treatment with aliphatic and aromatic acid chlorides gives thienones. The reaction is modified so that thiophene and the acid chloride are treated with a small amount of the chloromercuri compound which

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[1] Denigès, *Bull. soc. chim.* (3) 13 (1895), 538; (3) 15 (1896), 1064. *Ann. chim. phys.* (7) 18 (1899), 1420; (8) 12 (1907), 398.

[2] Volhard, *Ann.* 267 (1892), 176, 180. Steinkopf and Bauermeister, *Ann.* 403 (1914), 55. Finzi, *Gazz. chim. ital.* 45 II (1915), 283. *Chem. Zentr.* 1916 I 474. Steinkopf, *Ann.* 413 (1917), 318. *Chem. Abst.* 11 (1917), 2326.

[3] Volhard, loc. cit. 180.

acts as a catalyst. In this way the acid halides of the following acids have been employed: acetic, benzoic, o-toluic, p-toluic and p-nitrobenzoic. This reaction of acid chlorides with the C — Hg linkage to form a new C — C linkage is one which would be expected and which should prove useful in synthetic work. Unfortunately it appears to be confined to the thiophene series.

3. With arsenic chloride.

The reaction takes place readily on heating giving $R — AsCl_2$ and a small trace of R_2AsCl. The same product can be obtained by heating thiophene with arsenic trichloride using a trace of mercuric chloride as a catalyst.

4. With metallic sodium.

The chloride when heated in xylene solution with sodium gives the R_2Hg compound, α-mercury dithienyl. Yield 50%. This reaction is a good illustration of the ease of changing from R — Hg — X to R_2Hg in the thiophene series. Most C — Hg compounds react with metallic sodium giving metallic mercury.

5. With inorganic iodides.

An acetone solution of the chloride reacts with one molecule of a similar solution of sodium iodide to give a mixture of the corresponding iodide and mercury dithienyl. This is unusual as a large excess of iodide is ordinarily required to give the R_2Hg compound. If an excess of sodium iodide is used the yield of mercury dithienyl is almost quantitative. Apparently the tendency to form R_2Hg is so great in the thiophene series that the corresponding iodide as soon as formed tends to change to mercuric iodide and R_2Hg without any excess of sodium iodide to form a complex with the former substance.

α-Bromomercuri thiophene.

Is prepared by boiling mercury dithienyl and mercuric bromide in acetone solution. It is easily soluble in acetone, fairly soluble on heating in alcohol, chloroform, carbon disulfide, benzene and toluene. It is recrystallized from toluene in silvery leaflets. M.P. 169-70°; after sintering. (SHg).

α-Iodomercuri thiophene.

Is prepared from the chloride and one molecule of sodium iodide in acetone. The precipitate consists of sodium chloride and mercury dithienyl. When the filtrate is treated with water a white precipitate is formed. Later, some mercuric iodide separates. The silvery leaflets obtained by recrystallizing from alcohol are slightly red and become more so on rubbing when dry. The pure iodide can be obtained by dissolving mercury dithienyl and mercuric iodide in acetone and diluting with water. It then forms pure white crystals which are not changed by rubbing. Yield 90%. M.P. 117° (Hg). In concentrated solution an impure product is obtained. It is insoluble in water, slightly soluble in hot alcohol, little soluble in cold benzene, easily hot, fairly soluble in ether, soluble in cold acetone. The iodide tends to change to mercuric iodide and mercury dithienyl. It reacts even in the cold with arsenic triodide giving mercuric iodide.

α-Mercury dithienyl.

The best preparation is from an acetone solution of the chloride and an excess of sodium iodide. The white precipitate is washed with water to remove sodium chloride and the residue is dried and crystallized from benzene. M.P. 197°. Insoluble in water, hardly soluble in cold alcohol, not easily even hot, rather difficultly soluble in cold benzene and chloroform, easily hot, fairly soluble even in cold acetone. (Hg).

Mercury dithienyl reacts with the three mercuric halides in acetone solution giving thienyl mercuric halides in about 90% yields. In each case the acetone solution is diluted with water to precipitate the product. Mercury dithienyl reacts with arsenic trichloride spontaneously, forming mercuric chloride and the three possible substituted arsines. Primary and secondary alkyl halides do not react with mercury dithienyl.

However, tertiary butyl iodide reacts vigorously on gentle warming giving an oily peculiar smelling liquid which has not been purified.

Di-mercurated thiophenes.[4]

2-Acetoxymercuri-5-hydroxymercuri thiophene.

Is prepared by refluxing commercial benzene with mercuric acetate. After half an hour all of the thiophene has been removed forming a white precipitate. Thiophene reacts more easily than benzene. Thus, in a run which gave 32 gm. of the thiophene compound only .2 gm. of phenyl mercuric acetate was formed. It decomposes at 270°

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[4] Volhard, loc. cit. 177. Dimroth, *Ber.* 32 (1899), 759. *Chem. Zentr.* 1899 I 936. Schwalbe, *Ber.* 38 (1905), 2208. Steinkopf and Bauermeister, *Ann.* 403 (1914), 62.

without melting. It is soluble only in acetic acid from which it crystallizes slowly in very fine needles of the diacetate which loses acetic acid very easily. (CHHg). There seems to be some doubt about the nature of the original precipitate as it is found to contain only half the theoretical amount of sulfur.[5]

2, 5-Dichloromercuri thiophene.

Is prepared in the usual way from the acetate. It forms a white earthy powder which is insoluble in common solvents. It is not acted upon readily by acids, even by concentrated nitric acid. It gives no action with alkalies. (CHClSHg). It sinters at 265° and decomposes at about 275°. The dichloride reacts readily with iodine and water on warming forming di-iodothiophene. M.P. 40° (I). The reaction with bromine is not so smooth as an oily mixture of di-, tri-, and tetrabromothiophenes is formed.

Mercury Compounds of α-Monosubstituted Thiophenes.[6]

5-Chloromercuri-2-methyl-thiophene.

Is prepared from 2-thiotolene and mercuric chloride and sodium acetate. Most of the product separates in 13 hours. Yield 44%. It crystallizes from alcohol in shining crystals. M.P. 204°, after sintering. (CHClSHg). Warming the chloride with benzoyl chloride gives the corresponding phenyl ketone.

5-Chloromercuri-2-carboxyl-thiophene.

Is prepared in the usual way, from thiophene-2-carboxylic acid. On standing about ten days a yellow precipitate forms. Only part of this is soluble in ammonium hydroxide. If the residue is treated with sodium hydroxide it dissolves giving a solution from which dilute hydrochloric acid precipitates the chloride in a form soluble in ammonium hydroxide. It is practically insoluble in water and common solvents. The soluble and insoluble forms give the same analyses for mercury and sulfur. No explanation is known for the existence of these two forms.

5-Chloromercuri-2-phenyl-thiophene.

Is prepared in the usual way. After seven days the product is filtered off. The shining leaflets are recrystallized from a large volume

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[5] Schwalbe, loc. cit.

[6] Steinkopf and Bauermeister, loc. cit. 63. Volhard, loc. cit. 180. Steinkopf, loc. cit. 319.

of hot alcohol. M.P. 234°, not sharp. (Hg). It is very little soluble in cold alcohol and benzene and only difficultly soluble hot.

5-Halidemercuri-2-chlorothiophene.

The *chloride* may be prepared in the usual way from the substituted thiophene and mercuric chloride and sodium acetate. It is readily soluble in hot alcohol. Silvery leaflets. M.P. 213-9°, after sintering (SHg). It is insoluble in water and ligroin, difficultly soluble in cold alcohol, benzene, toluene, fairly soluble hot, soluble even in cold acetone. The *bromide* is prepared from the R_2Hg compound and mercuric bromide dissolved in hot acetone and cooled to give crystals. It is less soluble than the R_2Hg compound. Yield 93%. M.P. 191°. It is recrystallized from toluene, in felted white crystals. (SHg). The *iodide* may be prepared from the chloride by treatment with one molecule of sodium iodide. In this case none of the R_2Hg compound is formed.

5, 5′-Mercuribis-2-chlorothiophene.

Is prepared from the chloride in acetone with a little over two molecules of sodium iodide. The reaction takes place in the cold. The product forms silvery crystals from alcohol. M.P. 155°, after sintering. (SHg). It is fairly soluble in acetone and ethyl acetate, difficultly soluble in cold benzene and chloroform, easily on heating, very difficultly soluble in cold alcohol, fairly in hot, very little soluble in ligroin even on heating.

5-Halidemercuri-2-bromothiophene.

The *chloride* is prepared in the usual way. It forms small white needles from alcohol. M.P. 225°, after sintering. (SHg). It is insoluble in water, little soluble in ether, very difficultly in cold alcohol, fairly well in hot, little soluble in cold benzene and toluene, fairly on heating, fairly soluble in cold acetone. The *bromide* is prepared from the R_2Hg compound and mercuric bromide in acetone. White felted needles separate from a benzene solution. M.P. 197°, after sintering. (SHg). It is fairly soluble in acetone and ethyl acetate, difficultly in cold benzene, more soluble on heating, very difficultly soluble in cold alcohol, little soluble even on heating. The *iodide* is made from the chloride and one molecule of sodium iodide. In this case none of the R_2Hg componnd is added unless an excess of sodium iodide is used. It is easily soluble in carbon disulfide, acetone, and ethyl acetate, fairly soluble in benzene and toluene, little in cold alcohol and chloroform but easily on heating. It crystallizes from alcohol in small white crystals. It turns slightly red in light. M.P. 119° (SHg).

5, 5′-Mercuribis-2-bromothiophene.

It is prepared from the chloride and two molecules of sodium chloride in the least possible amount of acetone. It forms white felted crystals from benzene. M.P. 183°, after sintering. (SHg). It is difficultly soluble in cold benzene and chloroform, easily on heating, difficultly soluble in cold alcohol and little even when hot.

5-Halidemercuri-2-iodothiophenes.

The *chloride* is prepared in the usual way. The reaction takes three weeks. The product crystallizes from alcohol in fine felted crystals. It sinters at 215° and melts at 225° (SHg). It is insoluble in water and ligroin, very difficultly soluble in cold, and not readily even in hot alcohol and chloroform, little soluble in cold benzene and acetone, fairly soluble hot. Treated with acetyl chloride at about 90° it gives a poor yield of the corresponding methyl ketone. Treatment with iodine and water gives 2, 5-diiodothiophene. Treated with one molecule of sodium iodide it gives a mixture of the iodide and the R_2Hg compound. In this it apparently differs from the corresponding 2-chloro- and 2-bromothiophene derivatives. The *bromide* is made in the usual way from the R_2Hg compound and mercuric bromide. It is recrystallized rapidly from xylene (long boiling gives a violet color). The white felted needles darken at 170° (SHg). It is fairly soluble in acetone, difficultly in carbon disulfide and xylene, very difficultly in alcohol and benzene. The *iodide* is made from the R_2Hg compound and mercuric iodide in acetone. It is recrystallized from benzene and petroleum ether. It is a slightly yellow microcrystalline powder. M.P. 141-2°, giving a cloudy liquid which clears at 165°. It turns red on rubbing (possibly impure). (SHg). It is fairly soluble in acetone, difficultly in cold chloroform, benzene, xylene, but fairly soluble hot.

5, 5′-Mercuribis-2-iodothiophene.

The chloride is treated with more than two molecules of sodium iodide in acetone. It sinters at 200°, melts at 223-4°. It probably contains some of the corresponding iodide. It crystallizes from hot xylene in light yellow needles. M.P. 231°, after sintering. (SHg).

It is very difficultly soluble in common solvents, only dissolving in hot xylene.

Mercury Derivatives of 2, 5-Disubstituted Thiophenes.[7]

2, 5-Dimethyl thiophene reacts with mercuric chloride and sodium acetate in a different way from the thiophenes which have an alpha position unsubstituted. In this case a compound is formed which apparently results from the addition of a molecule of basic mercuric chloride to the double bond and the union of this molecule with a molecule of mercuric chloride. The evidence for this formulation is based on a mercury analysis and the fact that long boiling with alcohol gives 3-chloromercuri-2, 5-dimethyl thiophene. The formation of this intermediate compound suggests the possibility that all mercurations of aromatic compounds are preceded by similar additions to the double bonds of the nucleus. The 2, 5-dihalogen thiophenes give no reaction with mercuric chloride and sodium acetate even on very long standing in the cold. Heating causes the separation of calomel.

Compound of 2, 5-dimethyl-2-hydroxy-3-chloromercuri-2, 3-dihydrothiophene and $HgCl_2$.

Is prepared from 2, 5-dimethyl thiophene, mercuric chloride and sodium acetate. White crystals separate. After seven days the crystals are filtered and quickly recrystallized from hot alcohol. M.P. 186-7° after sintering. (Hg). Insoluble in water, very little soluble in ether, cold alcohol, chloroform, benzene, readily soluble in hot alcohol, chloroform and benzene, fairly soluble in cold acetone, easily hot. The mother liquor from the crystallization from alcohol when diluted with water gives 3-chloromercuri-2, 5-dimethyl thiophene. The same substance can be obtained by boiling the addition compound with alcohol for some time and cooling. The filtrate from the mercuric compound gives tests for mercuric ions.

3-Chloromercuri-2, 5-dimethyl-thiophene.

Is prepared from the mercuric chloride addition compound by long boiling with alcohol and cooling. M.P. 156-7°, after sintering. (SHg). It is insoluble in water, slightly soluble in cold alcohol easily hot, fairly soluble in cold ether and benzene, easily soluble in acetone.

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[7] Steinkopf and Bauermeister, loc. cit. 65.

The chloride reacts with sodium iodide even in excess, giving only the corresponding iodide and no trace of the R_2Hg compound. This behaviour is markedly different from that of the alpha mercurated compounds, which tend to form the R_2Hg compound even when only one molecule of sodium iodide is used. The R_2Hg compound can be made from the β-chloride by treatment with metallic sodium in xylene.

3-Iodomercuri-2, 5-dimethyl-thiophene.

Prepared from the chloride in acetone solution treated with sodium iodide. It crystallizes from benzene in white needles. M.P. 175°, after sintering. (Hg). It is fairly soluble in carbon disulfide, not easily in acetone, little in ethyl acetate and chloroform, difficultly in carbon tetrachloride, benzene and toluene, easily soluble in all of these solvents hot. Alcohol does not dissolve it readily even on heating.

3, 3′-Mercuribis-2, 5-dimethyl-thiophene.

It cannot be prepared from the chloride and an excess of sodium iodide. The chloride is shaken with xylene and sodium and the refluxed. The dark residue is filtered off and the filtrate is evaporated to a small volume. A brownish white residue separates. When purified by boneblack and crystallization from 70-120° ligroin it gives some of the unchanged chloride and a very small amount of the R_2Hg compound. M.P. 144-5° (S).

Mercury Derivatives of Beta-substituted Thiophenes.[8]

β-Methylthiophene reacts with mercuric chloride and sodium acetate forming mono- and di-mercurated products. The mercury atoms enter the alpha position. It has not been determined whether the mono-product has the mercury on the same side of the ring as the methyl group or not.

5(?)-Chloromercuri-3-methyl-thiophene.

Is prepared in the usual way. It is recrystallized from slightly diluted alcohol to separate it from the di-mercury compound. (ClSHg).

2-5-Dichloromercuri-3-methyl-thiophene.

A by-product in preparation of the mono compound. It is a white granular substance, insoluble in common solvents. It is only slightly attacked by acids, even by concentrated nitric acid. (ClSHg).

[8] Steinkopf, *Ann.* 403 (1914), 15. Volhard, *Ann.* 267 (1892), 182.

β-Isopropyl thiophene reacts with mercuric chloride and sodium acetate giving a mixture of mono- and di-mercurated products in the ratio of two to one by weight.

5(?)-Chloromercuri-2-isopropyl-thiophene.

It is recrystallized from alcohol in which the di-compound is insoluble. It forms white needles which are soluble in ether and insoluble in water. M.P. 137° (CHClHg).

2, 5-Dichloromercuri-3-isopropyl-thiophene.

It is separated from the mono-compound by extracting the latter with hot alcohol. The white granular residue is insoluble in all common solvents. It is only slowly attacked by nitric acid. (CHSClHg).

Mercury Derivatives of Beta-disubstituted Thiophenes.[9]

3, 4-Dimethyl-thiophene gives a mixture of mono- and di-mercurated products in the ratio of two to one. These are separated by hot alcohol which does not dissolve the di-compound.

2-Chloromercuri-3, 4-dimethyl-thiophene.

Is prepared in the usual way. The reaction mixture is filtered after fifteen hours. The hot alcohol extract gives crystals which melt 137-8°, after sintering. (SHg). It is only very slightly soluble in hot water, slightly soluble in cold alcohol, benzene, chloroform, easily on heating, soluble in acetone even in the cold. The corresponding *iodide* is made in good yield from the chloride by one molecule of sodium iodide in acetone. None of the R_2Hg compound is formed. Crystallization from benzene gives yellowish leaflets. M.P. 142°, after sintering. (SHg). It is easily soluble in carbon disulfide, fairly soluble in acetone and chloroform, difficultly soluble in cold benzene and toluene, easily hot, difficultly in alcohol.

2, 2′-Mercuribis-3, 4-dimethyl-thiophene.

Is prepared from the iodide and sodium iodide in acetone. Fair yield. It crystallizes from much alcohol in felted crystals. M.P. 155-6°, after sintering. (SHg). It is easily soluble in carbon disulfide and chloroform, fairly soluble in benzene and toluene, little in cold

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[9] D. R. P. 247,625. *Chem. Zentr.* 1912 II 166. Steinkopf and Bauermeister, *Ann.* 403 (1914), 63. Steinkopf, *Ann.* 413 (1917), 326. Chem. Abst. 11 (1917), 2326.

acetone, easily hot, difficultly in cold ligroin, very difficultly in cold alcohol, fairly hot.

2, 5-Dichloromercuri-3, 4-dimethyl-thiophene.

The residue, formed in the preparation of the mono-compound, is purified by repeated extractions with hot alcohol. It is insoluble in common solvents. (SHg). It does not melt at 270°.

Mercury Compounds of the Alkaloids.

Almost all alkaloids react with mercuric chloride and other mercuric salts forming crystalline, relatively insoluble compounds which are very useful in the separation and identification of these substances. These mercuric compounds are probably "molecular addition products." In all cases hydrogen sulfide gives the original alkaloid and mercuric sulfide.

Mercury Compounds of Pyridine and Related Substances.

Many addition compounds of mercuric salts with pyridine and similar substances are known.[9a]

Mercury Derivatives of Indole.[10]

3-Acetoxymercuri-1-methyl-indole.

Is prepared from N-methyl indole and mercuric acetate. It crystallizes from hot alcohol, benzene or acetone in fine needles.

3-Hydroxymercuri-1-methyl-indole.

Is insoluble in common solvents, soluble in alkalies. Hot mineral acids split the C — Hg linkage.

3-Hydroxymercuri-2-p-anisyl-indole is a brown precipitate.

A compound of two molecules of *3-hydroxymercuri-2-methyl-indole* and one molecule of mercuric acetate is known. It forms a yellow precipitate, insoluble in common solvents. It is soluble with decomposition in mineral acids. An aqueous suspension is only gradually blackened by hydrogen sulfide. This is remarkable as "molecular compounds" of this kind are usually blackened immediately by sulfides.

[9a] See Appendix D.

[10] D. R. P. 236,893. *Chem. Zentr.* 1911 II 404.

2-Methyl indole (Methyl ketole) gives a complex mercury compound with mercury fulminate and hydrochloric acid.[11]

3-Acetoxymercuri-2-methyl-1-phthalyl-indole.[12]

It is a slightly red precipitate, insoluble in common solvents. It is decomposed by hot dilute mineral acids.

Quinoline mercury compounds.

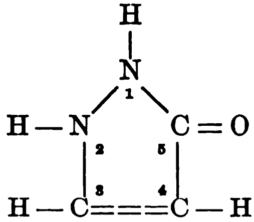
Mercury salts of quinoline sulfonic acid, carboxylic acids, and hydroxy acids are heated until alkali soluble.[13]

Acridine.

2, 7-Dimethyl-3, 6-diamino acridine treated with methyl chloride and mercuric halides gives a yellow brown powder soluble in water, alcohol, ethyl acetate, and acetic acid.[14]

N-Methyl-2, 7-dimethyl-3, 6-diamino acridine reacts with mercury compounds in suitable solvents giving a yellow brown powder soluble in water, alcohol, and insoluble in ether.

Mercury Derivatives of Pyrazolones.[15]



When phenyl-5-pyrazolones are treated with mercuric acetate in alcohol three or four acetoxymercuri groups are introduced into the molecule. From one to three of these may be in the phenyl group depending on the conditions and the other substituents in the pyrazolone ring. Substitution takes place in the benzene ring even when it is attached to the 3—C instead of the 1—N of the ring. The other acetoxymercuri groups are attached to carbon atoms 3 and 4. In most cases one of the groups takes the place of the hydrogen on the 4—C

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[11] König, *J. prakt. Chem.* (2) 84 (1911), 211.

[12] D. R. P. 236,893 loc. cit.

[13] D. R. P. 289,246. *Chem. Abst.* 10 (1916), 2500.

[14] U. S. Pat. 1,259,517. *Chem. Abst.* 12 (1918), 1496.

[15] Schrauth and Bauermeister, *Ber.* 47 (1914), 2736.

and the other together with an alkoxyl or hydroxyl group adds to the double bond between the 3 and 4 carbon atoms. If the original pyrazolone has no hydrogen atom on the 4 carbon (the carbon alpha to the ketone group), mercuration becomes more difficult. It is impossible in alcohol solution even on long boiling. This perhaps indicates that substitution in the 4 position precedes a shifting of the entering group to the benzene nucleus. If the group in the 4 position is a halogen or a methyl group, mercuration can be accomplished by heating the pyrazolone with mercuric acetate at 160°. Mercuration then takes place in the benzene ring and by addition of —HgOAc and —OH to the 3 and 4 positions respectively. If the 4 position is occupied by a dimethylamino group no mercuration is possible as the mercuric acetate oxidizes the compound when heated with it.

3-Methyl-3, 4-diacetoxymercuri-4-methoxy-1-acetoxymercuriphenyl-3, 4-dihydro-5-pyrazolone.

3-Methyl-1-phenyl-5-pyrazolone and mercuric acetate are mixed in *cold* methyl alcohol. The rhombic crystals are filtered after standing 24 hours. Yield 66%. Additional recovery by evaporating the mother liquor in vacuo raises the yield to 90%. The product is recrystallized from methyl alcohol. The crystals contain one molecule of water which can be removed in vacuo at the boiling point of xylene. (CHHg, H_2O). M.P. 167°, with slight decomposition. It is easily soluble in ethyl alcohol, soluble in ten volumes of methyl alcohol. Treatment with ammonium sulfide or dilute hydrochloric acid removes the mercury in position 4, leaving the mercury in position 3 and that attached to the benzene ring.

3-Methyl-3-chloromercuri-4-methoxy-1-chloromercuriphenyl-3, 4-dihydro-5-pyrazolone.

It is prepared by treating the above tri-acetoxymercuri compound with .25 N hydrochloric acid which removes the mercury in the 4 position. It is somewhat soluble in acetone. (CHClHg).

3-Methyl-3, 4-diacetoxymercuri-4-methoxy-1-diacetoxymercuriphenyl-3, 4-dihydro-5-pyrazolone.

It is prepared from the same 3-methyl-1-phenyl-5-pyrazolone and mercuric acetate, but by refluxing in methyl alcohol for three hours, and then evaporating to a small volume. It is difficultly soluble or entirely insoluble in the common solvents. It decomposes about 225° (CHHg).

When the phenyl group is attached to position 3 instead of to position 1 the mercuration takes place on the benzene ring and the 4 position but no addition of —HgOAc and —OH to the 3, 4 positions takes place. The change in the position of the phenyl group may cause a rearrangement so that the substance is a 5-hydroxy pyrazole instead of a 5-pyrazolone.

3-Diacetoxymercuriphenyl-4-acetoxymercuri-5-hydroxypyrazole.

It is prepared by refluxing 3-phenyl-5-pyrazolone with three moles of mercuric acetate in methyl alcohol. Any cloudiness is removed by adding a little acetic acid. The precipitate obtained on cooling is washed with methyl alcohol and ether and dried in vacuo. (CHHg). It is difficultly soluble in ethyl and methyl alcohols and in acetic acid. It forms colorless needle crystals. Ammonium sulfide gives mercuric sulfide. Decomposes at 250°. Treatment with hydrochloric acid removes the mercury in position 4 leaving a di-mercury compound.

3-Dichloromercuriphenyl-5-hydroxypyrazole.

This is prepared from the triacetoxymercuri compound and .25 N hydrochloric acid which removes the mercury in position 4. (CHCl Hg). It is insoluble in common solvents. It decomposes about 240° without melting. It is blackened by ammonium sulfide at once. This is unusual for a compound containing mercury attached to a phenyl group.

2, 3-Dimethyl-3, 4-diacetoxymercuri-4-methoxy - 1 - acetoxymercuriphenyl-3, 4-dihydro-5-pyrazolone.

When the phenyldimethylpyrazolone (antipyrine) is treated with two or three molecules of mercuric acetate no manageable product is obtained. Treatment with four molecules of mercuric acetate at 60° gives the pure tetramercurated product. Rhombic leaflets. Yield 97% (CHNHg). It sinters about 205° and then decomposes giving a gas. It is insoluble in most common solvents but slightly soluble in hot methyl and ethyl alcohols, especially in the presence of a trace of acetic acid. It is more soluble in water acidified with acetic acid, very soluble in presence of mercurated aromatic amines, ammonium hydroxide and amine bases such as ethylenediamine. Ammonium sulfide precipitates the mercury in position 4. Hydrochloric acid removes this mercury leaving the tri-mercurated product.

2, 3-Dimethyl-3-chloromercuri-4-methoxy-1-dichloromercuriphenyl-3, 4-dihydro-5-pyrazolone.

Prepared from the tetra-acetoxymercuri compound and .25 N hydrochloric acid shaken for 12 hours to remove the mercury in position 4. (CHClHg). The microcrystalline product is slightly soluble in acetone, insoluble in common solvents. It does not melt. Ammonium sulfide does not blacken it at once. The filtrate from the preparation is found to contain one-quarter of all the mercury originally in the tetramercurated compound.

2, 3-Dimethyl-3, 4-diacetoxymercuri-4-ethoxy-1-diacetoxymercuriphenyl-3, 4-dihydro-5-pyrazolone.

It is prepared in the same way as the methoxy compound mentioned above but in an ethyl alcohol solution. The reaction is slower than in methyl alcohol. Yield 97%. It forms fine colorless needles containing one molecule of water which can be removed over phosphorus pentoxide at 110°. Its solubilities are like those of the methoxy compound. (CHHg). Hydrochloric acid as usual removes the mercury in position 4.

2, 3-Dimethyl-3, 4-diacetoxymercuri-4-methoxy-1-(diacetoxymercuri-p-tolyl)-3, 4-dihydro-5-pyrazolone.

It is prepared from p-tolyl dimethyl pyrazolone and mercuric acetate in methyl alcohol at 60° (CHHg). No M.P. Ammonium sulfide gives HgS at once. Hydrochloric acid removes the 4 mercuri group.

2,3-Dimethyl-3-chloromercuri-4-methoxy-1-(dichloromercuri-p-tolyl)-3, 4-dihydro-5-pyrazolone.

The tetra-mercuri compound is treated with .25 N hydrochloric acid. (CHClHg). It is slightly soluble in acetone but practically insoluble in other common solvents. It is not blackened at once by ammonium sulfide.

3-Methyl-2-ethyl-3, 4-diacetoxymercuri-4-methoxy-1-diacetoxymercuriphenyl-3, 4-dihydro-5-pyrazolone.

Phenyl ethyl methyl pyrazolone and four moles of mercuric acetate are heated with methyl alcohol at 60° for two hours. Prismatic needles. Yield 95% (CHHg). It dissolves readily in water containing a trace of acetic acid when heated. It is also soluble in hot methyl and ethyl alcohol containing acetic acid. It is practically insoluble in other common solvents but is very soluble in ammonia and ethylenediamine. Decomposes above 200° without melting. Hydrochloric acid removes the mercury in the 4 position.

3 - Methyl - 2 - ethyl - 3-chloromercuri-4-methoxy-1-(dichloromercuri-phenyl-3, 4-dihydro-5-pyrazolone.

It is prepared from the tetra-mercury compound and .25 N hydrochloric acid shaken in the cold for 12 hours. The yield is almost quantitative. (Hg).

3-Methyl-2-ethyl-3, 4-diacetoxymercuri-4-methoxy-1-(diacetoxymercuri-o-tolyl)-3, 4-dihydro-5-pyrazolone.

Prepared in the same way as the corresponding phenyl compound. (CHHg). No M.P. It reacts in the usual way with ammonium sulfide and HCl.

3-Methyl-2-ethyl-3-chloromercuri-4 - methoxy - 1 -(dichloromercuri-o-tolyl)-3, 4-dihydro-5-pyrazolone.

It is prepared from the tetra-mercury compound and hydrochloric acid in the usual way. (Hg). It is slightly soluble in acetone but practically insoluble in other solvents. Ammonium sulfide does not give HgS at once.

2, 3, 4-Trimethyl-3-acetoxymercuri-4-hydroxy-1-triacetoxymercuri-phenyl-3, 4-dihydro-5-pyrazolone.

The phenyl trimethyl pyrazolone cannot be mercurated in methyl alcohol solution. This is apparently because the position alpha to the ketone group has no hydrogen. If the pyrazolone and four moles of mercuric acetate are heated without any solvent in an oil bath at 160°, mercuration takes place. The cooled product is extracted with alcohol and decolorized by animal charcoal. It is obtained as a colorless amorphous hygroscopic solid. M.P. 237° with decomposition. (CHHg). Dilute hydrochloric acid gives a tetrachloride. Apparently only mercury in the 4 position is easily removed by acid. Since the original mercury compound is formed by adding — HgOAc and — OH to a double bond it is unusual that acidification, even with dilute hydrochloric acid, does not regenerate the original double bond. The *tetrachloromercuri compound* obtained decomposes at 245° (Hg). It gives no immediate precipitate with ammonium sulfide.

2, 3-Dimethyl-3-acetoxymercuri-4-bromo-4-hydroxy-1-triacetoxymercuriphenyl-3, 4-dihydro-5-pyrazolone.

The absence of an α-hydrogen makes an easy mercuration impossible. If the phenyl-dimethyl-bromo-pyrazolone is heated half an hour at 160° with four moles of mercuric acetate, four mercury atoms are introduced into the molecule. The fusion is cooled and extracted with alcohol, decolorized, and precipitated with a large amount of ether. (CHHg). It is very hygroscopic, easily soluble in cold water, less soluble in methyl alcohol containing a little acetic acid. It decomposes at 225° giving a gas. Cold ammonium sulfide gives no reaction. On boiling it gives mercuric sulfide. Sodium chloride gives the *tetrachloromercuri compound.* Sodium hydroxide gives the corresponding *hydroxide.* This compound as formulated has an unusual grouping in the 4 carbon which has a bromide atom and an hydroxyl group attached to it.

3-Methyl-4-acetoxymercuri-5-chloro-1-phenyl-pyrazole.

It is prepared by refluxing phenyl-methyl-chloro-pyrazole with three molecules of mercuric acetate in methyl alcohol. Total yield 97%. It crystallizes from chloroform in prisms. (CHHg). It is easily soluble in water, alcohol and all common solvents except ether and petrol ether. M.P. 123°. Cold ammonium sulfide gives no action. Sodium chloride and sodium hydroxide give the corresponding *chloride* and *hydroxide.*

3-Methyl-4-chloromercuri-5-chloro-1-phenyl-pyrazole.

It is prepared from the acetate by sodium chloride. It crystallizes from acetone. M.P. 165°. It is readily soluble in all common solvents except ether and ligroin. (CHClHg).

Miscellaneous references on antipyrine.[16]

Phenylhydrazine reacts with mercuric oxide giving mercury diphenyl.[17] Ethylhydrazine gives a similar reaction forming mercury diethyl.

Mercury Derivatives of Pyrimidine.[18]

2, 6 - Dihydroxy - 4 - imino - 3, 4 - dihydropyrimidine-3-acetic acid changed to its sodium salt and treated with mercuric salts easily gives

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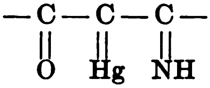
[16] Moulin, *Bull. soc. chim.* (3) 29 (1903), 201. Boehringer, *Chem. Abst.* 6 (1912), 1500. Scheitlin, *Chem. Abst.* 7 (1913), 2995. *Chem. Abst.* 13 (1919), 1126.

[17] E. Fischer, *Ann.* 199 (1879), 332. Allen, *J. Am. Chem. Soc.* 25 (1903), 421.

[18] D. R. P. 224,491. *Chem. Zentr.* 1910 II 608.

a compound which is formulated as having one mercury atom in place of the two hydrogen atoms in the 5 position. This grouping



$$-\underset{\underset{\textstyle O}{\|}}{C}-\underset{\underset{\textstyle Hg}{\|}}{C}-\underset{\underset{\textstyle NH}{\|}}{C}-$$

is peculiar enough to deserve further study.

Pyramidone reacts with mercuric chloride giving a white precipitate of microcrystalline needles.[19]

2-Methyl-4-quinazolone.

Gives a mercury compound when treated with fuming nitric acid and mercury which can be recrystallized from acetic acid. It forms a yellow powder which does not melt at 360°. Insoluble in common solvents. (N for $C_9H_7ON_2Hg$).[20]

Safranines gives complex mercury compounds.[21]

These do not react with sodium hydroxide and give only a slow action with ammonium sulfide on heating.

Acetoxymercuri benzidine is obtained as a white amorphous powder by boiling benzidine and mercuric acetate in dilute hydrochloric acid.[21a] The product is soluble in an excess of dilute acid.

Acetoxymercuri benzidine sulfonic acid and *acetoxymercuri benzidine disulfonic acid* have been prepared from 3-sulfobenzidine and 3, 3′-disulfobenzidine heated with mercuric acetate in water solution.[21a]

Cyclomercuripolymethylenes.[22]

Substances of this type are obtained by treating dibromides and di-iodides with dilute sodium amalgam. The products are usually polymerized forms of the simple compounds in which mercury is part of a closed ring. This tendency to polymerization is like that noted in analogous ring compounds containing oxygen or sulfur. The mercury ring compounds are harder to form than those containing oxygen and sulfur. Treatment of ethylene halides and trimethylene halides with sodium amalgam gives no organic mercury compounds.

1, 4-Diiodobutane reacts with 2% sodium amalgam forming a

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[19] Weehuizen, *Chem. Zentr.* 1906 II 1628.

[20] Bogert, *J. Am. Chem. Soc.* 34 (1912), 530.

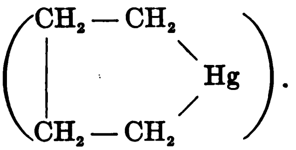
[21] D. R. P. 286,097. *Chem. Zentr.* 1915 II 569.

[21a] Private communication, G. W. Raiziss.

[22] v. Braun, *Ber.* 46 (1913), 1792. Hilpert and Grüttner, *Ber.* 47 (1914), 177, 183. v. Braun, *Ber.* 47 (1914), 491.

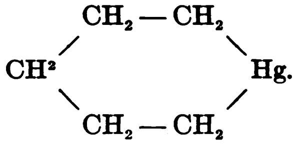
polymer of cyclo-mercuri-tetramethylene. 1, 5-Dibromopentane reacts with 1% sodium amalgam and ethyl acetate giving three compounds having the composition of cyclo-mercuri-pentamethylene. Compound 1 melts at 120° and is apparently only partly polymerized. Compound 2 melts at 41° and shows a molecular weight approximately four times that of the simple compound. Compound 3 is an oil having a molecular weight about six times that of the simple compound. The three compounds give the same products when treated with halogens or with mercuric halides.

Polymerized cyclomercuri-tetramethylene.



It is formed from the 1, 4 diiodide and 2% sodium amalgam and ethyl acetate. The product is easily soluble in ether. It is only partly volatile in a vacuum at 170°. It decomposes giving metallic mercury.

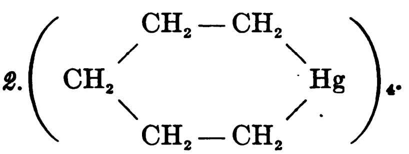
Cyclomercuri-pentamethylene, Compound 1.



The crude waxy mixture from the action of 1% sodium amalgam on the dibromide is extracted repeatedly with low boiling ligroin which dissolves compounds 1 and 3 leaving compound 2 as a slightly yellow fine powder. The extracts are allowed to evaporate spontaneously forming a large amount of colored oil and a small amount of compound 1 as white crystals. The oil on standing gives a small amount of compound 2. The remaining oil is compound 3. Compound 1 melts at 120°. It is recrystallized from a mixture of equal parts of benzene and 80° ligroin. It forms hard snow white crystals. (CHHg). M.W. average 360, calc. 270. It is easily soluble in cold ether and low boiling ligroin, also in benzene, difficultly soluble in water. Alcohol changes it to a smear without dissolving it. It is surprising that a cyclo-mercuri-pentamethylene should be a solid melting at 120°. The formation of a ring here apparently has a much more profound effect on the physical properties than it has in the case of oxygen, carbon, nitrogen or sulfur compounds.

By analogy to these compounds it would be expected to be a liquid boiling at about 210° as mercury diethyl boils at 159°.

Compound 2.



The residue insoluble in low boiling ligroin is dissolved in five volumes of benzene at 35°, filtered and overlayed with twice the volume of absolute ether and cooled in ice. The ether which evaporates is replaced. After a few hours a fine white powder separates which can be further purified by dissolving in 100 volumes of hot ether and evaporating in vacuo at 0° to one-quarter volume. The product is amorphous. It melts sharply at 41°, gives off a gas at 120° and foams suddenly at 124° (CHHg). M.W. average 1130, calc. 1080. It is almost insoluble in cold ether and low boiling ligroin, easily soluble even cold in chloroform, benzene and its homologs. Absolute alcohol gives a smear without dissolving it.

It reacts with bromine in carbon disulfide forming *1, 5-dibromomercuripentane.* M.P. 150° (CBrHg). The mother liquor gives a small amount of an oil containing bromine but no mercury. This is probably pentamethylene dibromide. Treatment with iodine in benzene gives a similar result. *1, 5-diiodomercuripentane.* M.P. 117°. White needles. (CHgI). The mother liquor gives a good yield of pentamethylene diiodide.

The compound reacts in benzene with ether solutions of mercuric halides giving white precipitates of the corresponding *1, 5-dihalidemercuri pentanes.* These are washed with ether and crystallized from benzene. *Chloride* M.P. 184° (Cl. & mixed M.P.). *Bromide* M.P. 150° (Br & mixed M.P.). *Iodide* M.P. 117° (I & mixed M.P.).

Compound 3. $[(CH_2)_5Hg]_6$.

The oil obtained from the petroleum ether extracts of the crude reaction product of pentamethylene dibromide and sodium amalgam does not crystallize even on standing for weeks in a vacuum over phosphorus pentoxide. (C high, Hg low). M.W. 1780, calc. 1620. The oil probably contains impurities which do not contain mercury. It reacts with bromine, iodine, and mercuric halides giving the same compounds, as those obtained from compound 2.

Mercuration of Azo Phenols and Azo Naphthols.[23]

If the position ortho to the phenolic hydroxyl is open treatment with mercuric acetate introduces the acetoxymercuri group. If both ortho positions are open it is possible to introduce two such groups. Among the compounds which cannot be mercurated even when fused with mercuric acetate are 2-benzeneazo-6-bromo-4-methyl phenol, 4-benzeneazo-2, 6-dibromo phenol, 2-benzeneazo - 4 - methyl - 6 - bromophenol.

Anhydro-2-hydroxymercuri-6-acetoxymercuri-4-benzeneazo-phenol.

The diacetoxymercuri compound cannot be obtained pure as it loses acetic acid even at room temperature. At 120° the change is complete and one molecule of acetic acid is removed leaving the anhydride. The product from refluxing azophenol with mercuric acetate in dilute acetic acid and alcohol is dissolved in hot acetic acid and poured into alcohol. The precipitate is dried at 120° (NHg). It does not melt at 300°. It is insoluble in hot water, slightly soluble in alcohol, chloroform, ethyl acetate, ethyl benzoate, benzene and nitrobenzene, moderately soluble in pyridine, readily soluble in acetic acid.

2, 6-Dichloromercuri-4-benzeneazo-phenol.

The above anhydro compound is boiled with a 5% potassium hydroxide and filtered. The filtrate is treated with saturated sodium chloride solution forming an orange red precipitate. When this is digested with hydrochloric acid it turns brick red. (NClHg). It does not melt at 300°. It is insoluble in common solvents, but slightly soluble in sodium hydroxide. It does not react with benzene diazonium chloride. The corresponding *dibromide* is made in the same way as the chloride. It is a brown red precipitate which does not melt at 300° and is insoluble in common solvents. (Br). No definite results are obtained by treating this substance with bromine.

2, 6-Diacetoxymercuri-4-tribromobenzeneazo-phenol.

It is prepared from the azophenol refluxed for six hours with mercuric acetate in dilute acetic acid and alcohol. The pink precipitate is recrystallized from acetic acid. (CHHgBrN). It does not melt at 300°. It is very difficultly soluble in common solvents, soluble in

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[23] Smith and Mitchell, *J. Chem. Soc.* 93 (1908), 845; 95 (1909), 1431. Schamberg, *Chem. Abst.* 11 (1917), 1690.

acetic acid. It is more stable than the corresponding benzeneazo compound but loses one molecule of acetic acid if heated at 120°.

2-Acetoxymercuri-4-methyl-6-benzeneazo-phenol.

The azophenol is treated with mercuric acetate. It is purified by dissolving in acetic acid and precipitating fractionally by addition of water. M.P. 269-70° (HgN). The compound is the same as that obtained from p-cresol mercuric acetate and benzene diazonium chloride.[24] The corresponding *chloride* is obtained by treating an acetic acid solution of the acetate with sodium chloride solution. It recrystallizes from a large volume of alcohol in yellow brown needles. M.P. 246-8° (HgCl).

2-Acetoxymercuri-6-nitro-4-benzeneazo-phenol.

Prepared by heating the azophenol with mercuric acetate in dilute acetic acid and alcohol on the steam bath for six hours. It crystallizes from acetic acid in pale yellow microcrystals. It does not melt at 300°. Insoluble in common solvents except acetic acid. (NHg). The corresponding *bromide* is made from an acetic acid solution of the acetate and potassium bromide. (Br).

The reaction of mercuric acetate with benzeneazonaphthols is naturally more complicated than that with the corresponding azophenols. 1-Benzeneazo-β-naphthol gives no mercury compound. On fusion with mercuric acetate it is oxidized to a ββ'dinaphthyl derivative. 4-Benzeneazo-α-naphthol gives a similar product with mercuric acetate. When 2, 4-disubstituted-α-naphthols are treated with mercuric acetate the acetoxymercuri group is introduced into the molecule, probably in the 8 position. The combinations of substituents used are di-benzeneazo, benzeneazo and nitro, and nitro and benzeneazo in the 2 and 4 positions respectively. If instead of the benzeneazo group a tribromobenzeneazo group is used no mercury compounds are obtained probably because of the extreme insolubility of the original substances.

8(?)-Acetoxymercuri-2, 4-dibenzeneazo-α-naphthol.

It is insoluble in common solvents. Softens at 218°, melts with decomposition at 235-8°. Acids remove the mercury. (CH).

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[24] Dimroth. *Ber.* 35 (1902), 2864.

8(?)-Acetoxymercuri-2-benzeneazo-4-nitro-α-naphthol.

Red amorphous product. M.P. 221-2° decomp. Insoluble in common solvents. (Hg).

8(?)-Acetoxymercuri-2-nitro-4-benzeneazo-α-naphthol.

Brick red powder. Soluble in hot glacial acetic acid which removes part of the mercury. (CHNHg). It darkens at 180°, melts at 208° with decomposition. The corresponding *chloride* is made by sodium chloride. It is insoluble in common solvents. It darkens at 130°, is black at 200°, does not melt at 270°.

Reaction of Diazonium Salts with Mercurated Phenols and Naphthols.[25]

Mercurated phenols couple with diazonium salts. If the p-position is unoccupied the mercury in the ortho position remains intact. If, however, the mercury is in the para position the coupling takes place there and the mercury is eliminated. Even in this case a small amount of the p-mercurated compound will couple in the ortho position leaving the mercury in the para position. The splitting off of the mercury to allow the coupling is suggestive of the reaction of p-hydroxybenzoic acid which loses carbon dioxide and couples in the para position when treated with benzenediazonium chloride. The reaction of diazonium salts with mercurated phenols is sometimes of use in determining the position of the mercury in the original compound. If the coupling results in the elimination of the organic mercury the latter was probably originally in the para position. o-Chloromercuriphenol couples with benzene diazonium chloride giving 2-chloromercuri-4-benzeneazo-phenol. p-Chloromercuriphenol gives mainly benzeneazophenol and mercuric chloride but also gives a small amount of 4-chloromercuri-2-benzeneazo-phenol. 2, 4-Dichloromercuriphenol has half of its organic mercury removed forming 2-chloromercuri-4-benzeneazo-phenol. Diazotized m-aminophenyl malachite green couples with o-chloromercuriphenol but no pure product is obtained. 2, 6-Dichloromercuri-4-benzeneazo-phenol will not react with benzene diazonium chloride. 2-Acetoxymercuri-p-cresol couples in the free ortho position giving 2-acetoxymercuri-6-benzeneazo-p-cresol. The *chloride* of this compound is obtained by precipitating by sodium chloride. It

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[25] Dimroth, *Chem. Zentr.* 1901 I 450. *Ber.* 35 (1902), 2044, 2860. Smith and Mitchell, loc. cit. 848. Reitzenstein and Bönitsch, *J. prakt. Chem.* (2) 86 (1912), 80.

crystallizes from much alcohol in fine yellow brown needles which gradually darken and melt at 249°, with decomposition. It is rather difficultly soluble in, alcohol, ether and benzene. (NCl).

A solution of an alkali salt of hydroxymercurisalicylic acid reacts with diazonium salt solutions in the cold giving water soluble compounds.[26]

Benzene diazonium chloride reacts with an alkaline solution of 1-acetoxymercuri-β-naphthol giving inorganic mercury and 1-benzene-azo-β-naphthol. Diazotized p-nitroaniline gives a similar reaction. The corresponding mercurated 6-sulfonic acid gives no action with ammonium sulfide but as soon as treated with a diazonium salt solution it gives mercuric sulfide showing that inorganic mercury has been liberated and that coupling has probably taken place. The anhydride of 1-hydroxymercuri-4-carboxy-β-naphthol couples with diazosulfanilic acid in the 1-position liberating inorganic mercury.

1-Hydroxymercuri-β-naphthylamine-6-sulfonic acid does not react with ammonium sulfide but as soon as it is treated with diazosulfanilic acid it forms a dye and a solution which immediately gives mercuric sulfide with sulfides.

Products Obtained by Diazotizing Mercurated Amines.[27]

o-Mercuribis-p-aminobenzoic acid can be diazotized and boiled in water solution to form the corresponding phenol, o-mercuribis-p-hydroxybenzoic acid. p-Acetoxymercuri aniline can be diazotized and coupled with a variety of aromatic compounds.

p-Acetoxymercuri-benzeneazo-phenol.

Diazotized p-acetoxymercuri aniline is treated with two molecules of phenol in 10% sodium hydroxide. After standing twelve hours the mixture is salted out with sodium acetate. The solid is dissolved in dilute sodium hydroxide and precipitated by acetic acid and then crystallized from acetic acid. It forms orange crystals melting at 218° (HgN). The alkaline solution dyes silk light yellow.

p-Acetoxymercuri-benzeneazo-resorcin.

It forms a very insoluble dark brown powder. It darkens at 160° and decomposes about 190° (HgN). An alkaline solution dyes silk orange.

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[26] D. R. P. 300,561. Fränkel, 665.

[27] Blumenthal and Oppenheim, *Biochem. Z.* 39 (1912), 51. Jacobs and Heidelberger, *J. Biol. Chem.* 20 (1915), 516.

p-Acetoxymercuri-p′-dimethylamino-azobenzene.

It is prepared by coupling the diazotized mercurated aniline with an acetic acid solution of dimethylaniline. It crystallizes from amyl alcohol in small brick red crystals. M.P. 215°. An acetic acid solution dyes silk bright yellow. It is difficultly soluble in common solvents except acetic acid which gives a bright red solution. (HgN). The corresponding *diethylamino compound* is made in a similar way. Recrystallized from absolute alcohol it forms glistening orange brown plates. It is more soluble than the dimethylamino compound. It turns red at 120° and melts at 154.5-156° (HgN).

1-amino-2-(p-acetoxymercuri benzeneazo)-5-napthalene sulfonic acid.

Is prepared by coupling diazotized p-acetoxymercuri aniline with α-naphthylamine-5-sulfonic acid. It decomposes about 280° (Hg).

(p-Acetoxymercuri-o-methylbenzeneazo)phenol.

It is prepared from diazotized p-acetoxymercuri-o-toluidine and phenol. It is recrystallized from 85% alcohol containing a trace of acetic acid. On rapid heating it melts at 205.5-6° (corr.), after softening. (HgN).

Mercuric salts and diazonium salts form stable double compounds.[28]

Albumen Compounds of Mercury.

Hemin mercury compounds.[29] Mercury compounds formed from horse hemoglobin and mercuric salts are soluble in dilute ammonium hydroxide and even in very dilute ammonium sulfide solution. They are less soluble in ammonium carbonate and sodium hydroxide.

Mercury compounds of *nucleic acids.*[30]

Mercury Derivatives of Aromatic Arsenicals.[31]

Many of the arsonic acids of aniline and phenol and their substitution products have been mercurated in the usual way. In most cases the structures assigned to the products have not been confirmed experi-

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[28] Hantzsch, *Ber.* 28 (1895), 1736.

[29] *Chem. Zentr.* 1914 II 1447.

[30] *Realenzyk. Pharm.* VI 486. Blumenthal and Oppenheim, *Biochem. Z.* 57 (1913), 288.

[31] Morgan, "Organic Compounds of Arsenic and Antimony," 1918, p. 183 ff. Bertheim, "Handbuch der organischen Arsenverbindungen," 1913, p. 132 ff. Brit. Pat. 12,472. (1908). Raiziss, Kolmer and Gavron, *J. Biol. Chem.* 40 (1919), 533.

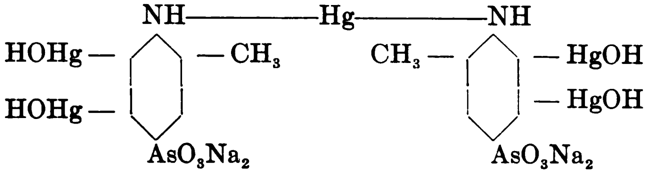
mentally. However, they are probably correct as most of the compounds which have been mercurated have positions ortho to the amino or hydroxyl group which are open. In all probability the acetoxymercuri group enters this position.

Arsanilic acid when treated with mercuric acetate and then with sodium hydroxide gives sodium salts of the acids, *3-hydroxymercuri-4-aminophenyl arsonic acid* and *3, 5-dihydroxymercuri-4-aminophenyl arsonic acid.* Treatment with sodium chloride gives the corresponding *chlorides* which are less soluble than the hydroxides.[32]

3-Acetoxymercuri-4-benzylaminophenyl arsonic acid forms a pale yellow amorphous powder. It is soluble in dilute alkali.[32a]

3-Acetoxymercuri-4-benzylamino-5-nitrophenyl arsonic acid separates as a yellow amorphous substance on heating solutions of mercuric acetate and the sodium salt of the benzylamino-nitrophenyl arsonic acid.[32a]

The arsonic acid of o-toluidine gives *3-hydroxymercuri-4-amino-5-methylphenyl arsonic acid.*[33] This arsonic acid also gives a complex compound which has received the name "Hydryl" and is believed to have the formula,



Apparently the positions of the mercury groups has not been proved.[34]

The arsonic acid obtained from o-nitroaniline reacts with mercuric acetate giving *3-acetoxymercuri-4-amino-5-nitrophenyl arsonic acid.*[35] This substance is soluble in acetic acid, 10 per cent hydrochloric acid, slightly soluble in methyl alcohol, insoluble in ethyl alcohol, ether, and methyl acetate. It reacts with ammonium sulfide giving an immediate precipitate of mercuric sulfide.

The arsonic acid of o-bromoaniline gives *3-acetoxymercuri-4-amino-5-bromophenyl arsonic acid.*[35] It is soluble in sodium hydroxide,

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[32] Brit. Pat., loc. cit.

[32a] Private communication, G. W. Raiziss.

[33] Brit. Pat., loc. cit.

[34] Jowett, see Morgan, loc. cit. 184.

[35] Raiziss et al., loc. cit.

10 per cent hydrochloric acid, and warm acetic acid. It reacts with cold ammonium sulfide. The corresponding *oxalyl* compound has been prepared.

p-Hydroxyphenyl arsonic acid when treated with mercuric acetate and then with sodium hydroxide gives a salt of *3, 5-dihydroxymercuri-4-hydroxyphenyl arsonic acid.*[36]

The arsonic acid of o-cresol gives *3-hydroxymercuri-4-hydroxy-5-methylphenyl arsonic acid.*[37]

The arsonic acid of o-nitrophenol gives *3-acetoxymercuri-4-hydroxy-5-nitrophenyl arsonic acid.*[38] It is soluble in sodium hydroxide, insoluble in methyl alcohol, ethyl alcohol, ether, methyl acetate, and acetic acid. It does not react at once with cold ammonium sulfide but does give mercuric sulfide after thirty minutes.

The position of the mercury in this compound is proved by treatment with iodine in potassium iodide solution. This gives 3-iodo-4-hydroxy-5-nitrophenyl arsonic acid. If the mercury compound is treated with a rather concentrated sodium sulfide solution it is converted to 3, 3′-mercuribis-4-hydroxy-5-nitrophenyl-arsonic acid. Sodium stannite is used as a reagent to test the completeness of the "bridging" reaction as it does not react with the R_2Hg compound but gives a precipitate of mercury if any of the $R — Hg — X$ compound remains.[39]

The arsonic acid of o, o′-dinitrophenol gives a mercury compound which is formulated as *2-acetoxymercuri-3, 5-dinitro-4-hydroxyphenyl arsonic acid.* It is partly soluble in sodium hydroxide, insoluble in methyl alcohol, ethyl alcohol, ether, and methyl acetate. It gives mercuric sulfide at once with cold ammonium sulfide.[40]

The arsonic acid of o-aminophenol gives *3-acetoxymercuri-4-hydroxy-5-aminophenyl arsonic acid.* It is soluble in sodium hydroxide with decomposition. It is slightly soluble in acetic acid and 10 per cent hydrochloric acid. It is insoluble in other solvents.[40] It does not give mercuric sulfide until digested with ammonium sulfide for thirty minutes at 80°.

The arsonic acid of o-acetaminophenol gives *3-acetoxymercuri-4-hydroxy-5-acetaminophenyl arsonic acid.*[40a] (N). It forms a brown

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[36] Brit. Pat., loc. cit.

[37] *Ibid.*

[38] Raiziss et al., loc. cit.

[39] Stieglitz, Kharasch, and Hanke, *J. Am. Chem. Soc.* 43 (1921), 1185.

[40] Raiziss et al., loc. cit.

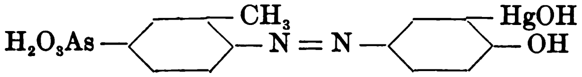
[40a] Private communication, G. W. Raiziss.

amorphous mass which is soluble in dilute sodium hydroxide but is insoluble in the usual organic solvents and in dilute acids.

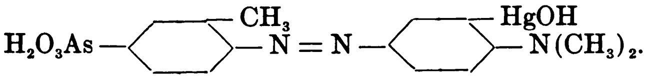
The arsonic acid of o, o′-diaminophenol gives *2-acetoxymercuri-3, 5-diamino-4-hydroxyphenyl arsonic acid.* This resembles the corresponding compound from o-aminophenol. It reacts with ammonium sulfide only on heating at 80° for thirty minutes.[41]

p-Benzarsonic acid gives a compound containing one acetoxymercuri group. It has not been determined whether this group is ortho to the carboxyl group or to the arsonic acid group. The compound is soluble in dilute hydrochloric acid, concentrated sodium chloride solution, insoluble in sodium hydroxide and organic solvents. It gives mercuric sulfide at once.[41]

The azo compounds obtained from the diazotized arsonic acid of o-toluidine and phenol or dimethyl aniline have been mercurated forming the compounds,



and



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[41] Raiziss et al., loc. cit.
[42] Brit. Pat., loc. cit.

APPENDIX A.

Analysis of Organic Mercury Compounds.

I. Analysis for Mercury.

A. Determination as the metal.

1. Collection of mercury during the analysis for carbon and hydrogen.[1]

The original device was to constrict the combustion tube in two places and condense the mercury in the space between them. After the combustion this piece of tubing was broken off, weighed, freed from mercury by heating, and weighed again. Grignard and Abelmann improved this arrangement by using a separate tube containing gold foil or fine wire to catch the mercury. Gold coated asbestos has been recommended for this purpose. (Werder.)

2. Collection of mercury from the substance heated with lime, etc.[2]

In this method the compound to be analyzed is mixed with lime, magnesite, sodium carbonate and similar substances. The metallic mercury is distilled out in various ways and condensed in constricted tubes, tubes containing gold foil, or on gold surfaces of various kinds. The method used in the writer's laboratory involves the condensation of the mercury on the inside of a specially designed gold crucible.[3]

3. Collection of mercury formed by the action of metallic sodium and alcohol.[4]

Some organic mercury compounds when dissolved in alcohol react with metallic sodium or with the hydrogen formed from its action on the alcohol giving metallic mercury. The globule of mercury is collected, washed, dried, and weighed in the usual way.

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[1] A. W. von Hofmann, *Ann.* 47 (1843), 63. Frankland and Duppa, *J. Chem. Soc.* 16 (1863), 415. *Ann.* 130 (1864), 107. Erdmann and Marchand, *J. prakt. Chem.* (2) 31 (1885), 393. Grignard and Abelmann, *Bull. soc. chim.* (4) 19 (1916), 25. *Chem. Abst.* 10 (1916), 1486 (cut of apparatus). Werder, *Z. anal. Chem.* 39 (1900), 358.

[2] Wertheim, *Ann.* 51 (1844), 304. Brandis, *Ann.* 66 (1848), 269. Hinterberger, *Ann.* 82 (1852), 317. Hofmann, *Ber.* 31 (1898), 1907; 32 (1899), 878; 33 (1900), 1335; 33 (1900), 1347, 1355, 1361, 2699. Sand, *Ber.* 34 (1901), 1338. Werder, *Z. anal. Chem.* 39 (1900), 358.

[3] See below.

[4] Schoeller and Schrauth, *Ber.* 53 (1920), 641.

4. Formation of the metal by direct electrolysis of a solution of the organic mercury compound.[5]

A few organic mercury compounds which are soluble in alkali can be electrolyzed directly in alkaline solution. Of course the organic compound can be decomposed by acid and the resulting solution can be electrolyzed.

B. Determination of mercury by iodimetry.[6]

C. Determination of mercury by precipitation methods.

The organic mercury compound must first be decomposed to give inorganic mercuric salts. The method of treatment depends on two things, (a) the stability of the C — Hg linkage, and (b) the nature of the organic residue left after the decomposition. In some cases warming with dilute acid will remove all of the mercury in inorganic form. In others vigorous treatment with acid oxidizing agents is necessary. In extreme cases the mercury compound must be decomposed by fuming nitric acid in a sealed tube at a high temperature. This process must be used carefully as some organic mercury compounds decompose explosively in contact with the nitric acid. In these cases it is advisable to heat the tubes in vertical position for some hours so that the decomposition takes place without actual contact between the substance and the liquid acid. After this preliminary heating the tubes are allowed to cool and then heated in the usual horizontal position.[7] Unless the organic products are completely oxidized they may interfere with the precipitation or may contaminate the precipitate formed. In some cases mercuric sulfide may be freed from such impurities by extraction with pyridine.[8] Among the oxidizing agents used are the following: nitric acid, aqua regia, bromine water, acid permanganate, and acid dichromate.[9]

The solution resulting from the decomposition contains inorganic mercury which can be determined by any of the usual methods. The purification of the mercuric sulfide precipitate by extraction with pyridine has been mentioned. The filtration of the mercuric sulfide

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[5] Sand and Singer, *Ber.* (1902), 3170.

[6] Sakurai, *J. Chem. Soc.* 37 (1880), 658. Brieger, *Chem. Zentr.* 1912 I 753.

[7] Hilpert and Grüttner, *Ber.* 48 (1915), 911.

[8] Manchot, *Ann.* 421 (1920), 321.

[9] Gerhardt, *Ann.* 80 (1851), 111. Hofmann, *Ber.* 31 (1898), 1905. Hofmann and Sand, *Ber.* 33 (1900), 1350, 2697. Rupp and Kropat, *Apoth. Ztg.* 1912, p. 377. Brieger and Schulemann, *J. prakt. Chem.* (2) 89 (1914), 131. Hilpert and Grüttner, loc. cit. Whitmore, *J. Am. Chem. Soc.* 41 (1919), 1848. Schoeller and Schrauth, *Ber.* 53 (1920), 634. White, *J. Am. Chem. Soc.* 42 (1920), 2359.

is facilitated by having a piece of quantitative filter paper under the asbestos matte in the Gooch crucible.[10] The inorganic mercury solution may be treated with a zinc thiocyanate solution to precipitate the complex thiocyanate of zinc and mercury.[11]

II. Analysis for Halogens.

A. After decomposition of the organic mercury compound in solution.

Of course the halogen cannot be determined by any of the usual methods until the mercury has been removed from the solution. If this is done by precipitation as the sulfide the halogen may be determined in the filtrate in the usual way.[12]

B. After decomposition by heating the solid mercury compound with lime, etc.

The decomposition mixture from which mercury has been removed by distillation is treated with nitric acid and precipitated by silver nitrate with the usual precautions.[13]

C. After treatment with hot sodium carbonate solution.

In some cases the organic mercury compound can be boiled with sodium carbonate and the halogen can be determined in the filtrate by the method of Volhard. This method is successful only when the mercury remains in the precipitate either in the form of the oxide or an insoluble organomercuric oxide. The fact that many of these substances are water soluble limits this method.[14]

III. Analysis for Carbon and Hydrogen.

The combustion of organic mercury compounds must be carried out in such a way that the mercury is completely removed before the combustion products reach the absorption train. This is probably best done by means of the device of Grignard and Abelmann.[15] If it is not desired to determine the mercury quantitatively it may be retained by gold foil, leaf, wire, or gold coated asbestos in the end of the combustion tube itself. Another device is to use a long combustion

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[10] White, loc. cit.

[11] Hart and Hirschfelder, *J. Am. Chem. Soc.* 42 (1920), 2684.

[12] Kutscheroff, *Ber.* 17 (1884), 14. *Z. anorg. Chem.* 14 (1898), 326. Whitmore, loc. cit.

[13] Pringsheim, *Ber.* 41 (1908), 4267. Kohn and Ostersetzer, *Z. anorg. Chem.* 80 (1913), 218. Schrauth and Bauerschmidt, *Ber.* 47 (1914), 2740. Lederer, *Ber.* 47 (1914), 279.

[14] Biilmann, *Ber.* 33 (1900), 1648.

[15] Loc. cit.

tube in two furnaces with a cooler section between in which the mercury condenses.[16]

IV. Analysis for Acetate.

Since mercuric acetate is the commonest mercurating agent the determination of the acetate group is often useful. This is done by treatment with phosphoric acid followed by steam distillation. The acetic acid in the distillate is titrated.[17]

V. There are also a number of articles on the general analysis of mercury compounds.[18]

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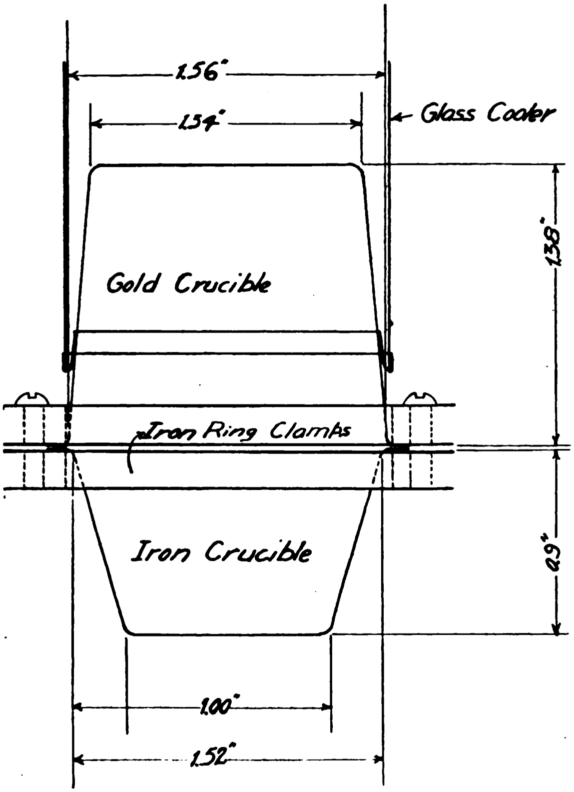
[16] Gerngross and Kersasp, *Ann.* 406 (1914), 247. Miscellaneous references on the combustion of organic mercury compounds. Nicholson, *J. Chem. Soc.* 3 (1851), 321. *Ann.* 62 (1847), 79. Dünhaupt, *J. prakt. Chem.* (1) 61 (1854), 399. Frankland and Duppa, *Ann.* 130 (1864), 107. Cowper, *J. Chem. Soc.* 39 (1881), 242. Erdmann and Marchand, *J. prakt. Chem.* (2) 31 (1884), 393. Dimroth, *Ber.* 32 (1899), 759. Sand and Genssler, *Ber.* 36 (1903), 3706. Anschütz, *Ann.* 359 (1908), 202. Schoeller, Schrauth, and Struensee, *Ber.* 44 (1911), 1048. Hilpert and Grüttner, *Ber.* 48 (1915), 911. Manchot and Haas, *Ann.* 399 (1913), 135. Gerngross and Kersasp, loc. cit. Grignard and Abelmann, loc. cit.

[17] Brieger and Schulemann, loc. cit. White, *J. Am. Chem. Soc.* 42 (1920), 2355.

[18] *Z. analyt. Chem.* 17 (1878), 526; 39 (1900), 358; 40 (1901), 534. *Compt. rend.* 116 (1893), 584. *Bull. soc. chim.* (3) 9 (1893), 504. *Gmelin-Kraut-Friedheim-Peters Handbuch d. anorg. Chem.* V-II 462. *Chem. Ztg. Rep.* 10 (1886), 216. *J. Chem. Soc.* 87 (1905), 431, 1878; 103 (1913), 513. *Analyst,* Oct., 1919. *J. Ind. Eng. Chem.* 2 (1910), 481. *Chem. Abst.* 7 (1913), 536, 896, 3979; 12 (1918), 739. *Ber.* 38 (1905), 2209. *Biochem. Z.* 36 (1911), 291. *Chem. Zentr.* 1889 II 391; 1911 II 722; 1912 II 151.

Determination of Mercury as the Metal.



The method for the determination of mercury in organic compounds which has proved most satisfactory in the author's laboratory is a modification of the ordinary method of heating the compound with lime and collecting the metallic mercury.[19] The only disadvantage is the initial cost of the gold crucible. However, the method is so much more rapid than the ordinary methods of determining mercury that the time saved warrants the expense.

Apparatus.

As shown in the accompanying diagram the apparatus consists of a gold crucible and an iron crucible each with a flange at the mouth.

[19] The apparatus was designed and the details of the process were worked out by Mr. V. E. Meharg, Research Assistant, under a grant from the U. S. Interdepartmental Social Hygiene Board, Dr. T. A. Storey, Secretary.

The iron crucible must be slightly smaller at the mouth than the gold crucible. The two crucibles are held together by two heavy iron rings which are drawn tightly together by four screws. The dimensions given in the diagram give a gold surface sufficient for the accurate amalgamation of quantities of mercury up to 0.12 gm. The dimensions indicated need not be exactly copied except the difference between the mouth diameters of the crucibles. As has been mentioned the iron crucible must be slightly smaller. If this is not the case there will be losses of mercury by its vapor working into the joint between the flanges. Then, when the crucibles are separated some mercury will adhere to the iron crucible and be lost. If it chances that no iron crucible of proper dimensions can be obtained it is possible to use a larger one by setting a smaller crucible inside of the larger one. This crucible must be tall enough to reach a little above the level of the flanges. The iron crucible should be set in an exactly fitted hole in a heavy asbestos board. This prevents the gold crucible from getting too hot. The gold crucible is cooled by means of a water jacket made of a large piece of glass tubing fitted to the crucible by means of a piece of thin-walled rubber tubing such as that used with Gooch crucibles. The glass tube is fitted with a two hole stopper and water circulated through it. The circulation of water must not be too rapid as the gold amalgamates best if kept between 50° and 90°. Another method of circulating water is the constant level siphon device used on water baths. In this case the top of the cooling tube is left open.

Method of Analysis.

The organic mercury compound is weighed in the iron crucible (in the small inner one if two are used), and thoroughly mixed with five times its weight of finely powdered anhydrous sodium carbonate. In some cases powdered barium peroxide must be added to insure complete oxidation . This is not usually necessary. The mixture is covered with a thin layer of anhydrous sodium carbonate and then with ten to twenty parts of dry powdered barium carbonate. In cases in which an unusually large amount of water is formed a layer of powdered barium oxide may be put in before the barium carbonate is added.

The iron crucible is now fitted to the gold crucible, the rings are put in place and the flanges of the two crucibles are brought tightly together by means of the four screws. The bottom of the iron crucible is put through the hole in the asbestos board and the cooling device is fitted to the gold crucible. The bottom of the iron crucible is then heated very gently. Almost all failures in this method of analysis are due to too rapid or too high heating. The heat used is gradually increased. Thirty minutes heating is sufficient. After a few trials it is easy to adjust the heating for a given set of crucibles. At the end of the heating the gold crucible is disconnected. The flange should be examined carefully for any traces of amalgam. If any are detected there has probably been a loss of mercury. The amalgam is rinsed carefully with alcohol and dried in a vacuum desiccator. It is then weighed. After weighing, the mercury is removed by heating the gold crucible gently in a Bunsen flame. It is then cooled in a desiccator. It is then ready to be weighed for another run. A complete mercury analysis may be run by this process in two and a half hours. Close supervision is needed during only a small portion of this time.

Halogens do not interfere with the process except in the case of some iodomercuri compounds. In the case of some of these compounds iodine sublimes on the amalgamated gold crucible and probably reacts with the mercury to some extent. The escape of the iodine is prevented by a layer of powdered sodium hydroxide placed under the barium carbonate layer.

A determination of halogen in the residue may be made by transferring it quantitatively to a suitable vessel, adding nitric acid, and then precipitating by silver nitrate solution in the usual way. Of course, the materials used must be halogen free.

APPENDIX B.

Proprietary Mercurials.

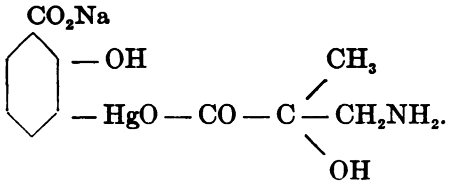
Afridol. The sodium salt of o′-hydroxymercuri-o-toluic acid.[1]

Anogon. A mixed mercurous and mercuric compound of diiodophenol sulfonic acid ("Sozoiodol"). It is formulated as $Hg-O-C_6H_2I_2-SO_3-HgI$.[2] It is also called Meriodin.

Aspirochyl. Mercuric salt of atoxyl (p-arsanilic acid).[3]

Asterol. Mixture of ammonium tartrate with the mercuric salt of p-phenol sulfonic acid.[4]

Asurol. A water soluble compound of anhydro mercurisalicylic acid and the sodium salt of α-hydroxy-β-aminoisobutyric acid.[5] It probably has the formula,



Asyphil. Mercuric salt of atoxyl. Same as Aspirochyl.[6]

Atoxiphil. A mercury compound derived from the anilide of meta-arsenic acid, $C_6H_5NH-AsO_2$.[7]

Contraluesin. It contains arsenic and mercury in combination or mixture with sozoiodol, quinine, and salicylic acid.[8]

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[1] *Biochem. Z.* 33 (1911), 399. *Chem. Zentr.* 1911 I 695, II 1877.

[2] D. R. P. 245,534. Fränkel, 674.

[3] *Chem. Zentr.* 1909 II 739, 1817.

[4] Fränkel, 674.

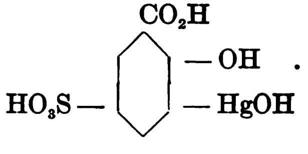
[5] *Therap. Monatsh.* 23 (1909), 4. *Chem. Zentr.* 1910 I 948. *Biochem. Z.* 32 (1911), 509; 33 (1911), 387; 57 (1913), 260. Fränkel, 664. Note.—Fränkel makes the statement that asurol is the sodium compound of hydroxymercurichlorophenoxyacetic acid. This is apparently an error.

[6] *Chem. Zentr.* 1908 II 1891.

[7] *Chem. Zentr.* 1908 II 1898.

[8] *Münch. med. Wochenschr.* 60, 62. *Chem. Abst.* 7 (1913), 863. *Biochem. Z.* 65 (1914), 468.

Embarin. Anhydride of hydroxymercuri sulfosalicylic acid,



The preparation appears as a liquid containing one-half of one per cent of acoin.[9]

Enesol. This substance is variously described: (1) A mechanical mixture of anhydro mercurisalicylic acid and arrhenal, CH_3 — AsO $(ONa)_2$. (2) An "acid salicyl ester of arsenic acid in which the three hydroxyl groups are replaced by mercury." (3) The mercuric salt of 3-carboxy-4-hydroxyphenyl arsonic acid.[10]

Hermophenyl. Mercury sodium salt of phenol disulfonic acid.[11]

Hydrargyroseptol. "Quinosol-mercury" and sodium chloride, "C_9H_6NO — $SO_3Hg.2NaCl$."[12]

Hydrargyrol. Mercuric salt of p-phenol sulfonic acid. It is used in "Asterol."[13]

Hydryl. The product from the action of mercuric oxide on the monosodium salt of 3-methyl-4-acetaminophenyl arsonic acid (Orsudan) is formulated as a salt of N-Mercuribis-(3-methyl-4-amino-5, 6-dihydroxymercuriphenyl arsonic acid).[14]

Levurargyre. A mercury compound prepared from nucleic acid from beer yeast.[15]

Levuretin. A mercury preparation with "completely masked" mercury.[16]

Meracetin. Anhydro mercuripyrocatechinacetic acid. It is probably the anhydride or inner salt of 3-hydroxymercuri-2-hydroxyphenoxyacetic acid.[17]

Mergal. Mercuric cholate, $Hg(C_{24}H_{39}O_5)_2$.[18]

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[9] *Biochem. Z.* 57 (1913), 267. Fränkel, 663, 666.

[10] *Ber.* 41 (1908), 933. *Biochem. Z.* 57 (1913), 260. *Chem. Abst.* 10 (1916), 951. Fränkel, 663. *Realenzyk. Pharm.* VI 562. Morgan, "Organic Compounds of Arsenic and Antimony," 1918, p. 198.

[11] *Biochem. Z.* 32 (1911), 59.

[12] *Realenzyk. Pharm.* VI. 457.

[13] Thorpe, *Dictionary of Applied Chem.* III 454.

[14] Morgan, 184.

[15] *Realenzyk. Pharm.* VIII 183.

[16] *Ibid.*

[17] Fränkel, 664.

[18] *Merck's Index,* 1907, p. 283. Fränkel, 667.

Mercurochrome-220. Hydroxymercuridibromofluorescein.[19]

Mercurol. A mercury nucleinate.[20]

Mercurophen. Sodium compound p-hydroxymercuri-o-nitrophenol.[21] It is also known as "No. 99."

Merlusan. A mercury tyrosin compound.[22]

Novasurol. A combination of the sodium salt of hydroxymercurichlorophenoxyacetic acid and diethyl barbituric acid.[23]

Phenegole. (Egole.) Mercuric salt of o-nitrophenol-p-sulfonic acid.[24]

Providol. Sodium compound of o, p-dihydroxymercuriphenol.[25]

Sublamin. A double compound of mercuric sulfate and ethylene diamine.[26]

Toxynon. Sodium salt of hydroxymercuriacetaminobenzoic acid.[27]

Upsalan. Sodium compound of p-hydroxymercuri-o-chlorophenol.[28]

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[19] *J. Am. Chem. Soc.* 42 (1920), 2359. *J. Am. Med. Assn.* 73 (1919), 1483.

[20] *Realenzyk. Pharm.* VIII 619.

[21] Fränkel, 665.

[22] *Ibid.*, 661.

[23] *Ibid.*, 664.

[24] *Realenzyk. Pharm.* IV 504.

[25] Fränkel, 659.

[26] *Gazz. chim. ital.* 39 I (1909), 143.

[27] *Biochem. Z.* 57 (1913), 260. Fränkel, 664. Note.—This substance is given a formula in which the carboxyl and acetamino groups are in the meta position. It is thus 2-hydroxymercuri-5-acetaminobenzoic acid. As a substance of this structure would be rather difficult to make it is possible that it may be a derivative of p-aminobenzoic acid instead of the meta acid.

[28] Fränkel, 659.

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(6) 22 (1905), 107, 247; (6) 24 (1906), 21; (6) 25 (1907), 423; (6) 26 (1907), 300; (6) 30 (1909), 145; (7) 6 (1912), 433; (7) 11 (1915), 279; (7) 15 (1917), 33, 241.
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Pharm. Ztg. 46 (1901), 352, 915; 54 (1909), 17, 310, 989, 1026; 55 (1910), 284, 558, 725; 56 (1911), 34, 75, 558, 605, 636, 738, 903; 57 (1912), 1031; 60 (1916), 724.
Neues Repert. Pharm. 17 (1868), 257; 22 (1873), 65.
Repert. Pharm. 4 (1893), 28.
Schweiz. Woch. Pharm. 47 (1909), 177.
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See also references to *Biochemische Zeitschrift* and *Zeitschrift für physiologische Chemie* in Appendix D, "Miscellaneous References."

APPENDIX D.

Supplementary Bibliographical Lists.

Mercury-Nitrogen Compounds.

The only organic compounds containing the Hg — N linkage which have been carefully studied are the mercury compounds of the acid amides and imides. These substances dissolve mercuric oxide readily giving N — Hg compounds. These substances behave like mercuric salts except that they do not react readily with bases. Sulfides give mercuric sulfide. Inorganic halides break the N — Hg linkage according to the equation

$$> N - Hg - N < + 2NaX + 2H_2O \rightarrow 2 > NH + 2NaOH + HgX_2.$$

Sodium thiosulfate produces a similar change. Acids give mercuric salts and the original amide or imide.

Mercury acetamide.
- *Ann.* 103 (1857), 324.
- *Ann. chim. phys.* (3) 52 (1858), 506.
- *Ber.* 7 (1874), 624; 23 (1890), 1553; 26 (1893), 423, 987.
- *Chem. News.* 78 (1898), 250.
- *J. Chem. Soc.* 73 (1898), 791.
- *Ber.* 32 (1899), 1358.
- *Z. physik. Chem.* 28 (1899), 392; 42 (1903), 690.
- *Monatsh.* 23 (1902), 1147.
- *J. Am. Chem. Soc.* 28 (1906), 1025.

Miscellaneous N-Hg compounds.
- *Am. Chem. J.* 18 (1896), 542.
- *Ann.* 130 (1864), 203.
- *Chem. Abst.* 5 (1911), 3880.
- *Chem. Zentr.* 1895 II 226; 1913 II 324.
- *Compt. rend.* 112 (1891), 997.
- *Ber.* 5 (1872), 382; 7 (1874), 624; 17 (1884), 133; 23 (1890), 1553; 26 (1893), 985; 33 (1900), 2228; 35 (1902), 1310, 2721; 45 (1912), 1731.
- *Biochem. Z.* 33 (1911), 381.
- *Bull. soc. chim.* (3) 11 (1894), 573; (3) 15 (1896), 863.
- *Gazz. chim. ital.* 27 I (1897), 567; 28 II (1898), 122, 434; 39 I (1909), 143.
- *J. Chem. Soc.* 91 1907), 1045.
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- *Merck's Index* 1907, pp. 278, 281.
- "Realenzyk. Pharm." VI 486.
- *Z. anorg. Chem.* 15 (1897), 208.
- *Z. Chem.* (2) 4 (1868), 303.
- *Z. physik. Chem.* 11 (1893), 466; 28 (1899), 385; 42 (1903), 690.

Sulfur-Mercury Compounds.
- *Ann.* 11 (1834), 3, 17; 51 (1844), 303; 72 (1850), 19; 119 (1861), 146; 120 (1861), 64; 136 (1865), 77; 140 (1866), 87; 146 (1868), 148; 154 (1870), 122, 179; 241 (1887), 117; 267 (1892), 173; 359 (1908), 202; 371 (1909), 201.
- *Ann. Spl.* 4 (1865), 97.

- *Ber.* 1 (1868), 172; 2 (1869), 544; 7. (1874), 648; 15 (1882), 125; 48 (1915), 1427; 53 (1920), 568, 1670, 1737.
- *Bull. soc. chim.* (4) 9 (1911), 532; (4) 17 (1915), 353.
- *Chem. Zentr.* 1908 I 1491.
- *Compt. rend.* 70 (1870), 626.
- *J. prakt. Chem.* (1) 53 (1851), 380; (2) 15 (1877), 205; (2) 84 (1911), 750.
- *Monatsh.* 10 (1889), 883.
- *J. Chem. Soc.* 95 (1909), 1918; 101 (1912), 935.
- *Z. anal. Chem.* 34 (1895), 457.
- *Z. anorg. Chem.* 6 (1894), 248; 14 (1897), 295; 17 (1898), 29.
- *Z. physik. Chem.* 11 (1893), 466.

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- Methyl alcohol. *Z. anorg. Chem.* 53 (1907), 327.
- Glycerol. *J. prakt. Chem.* (2) 55 (1897), 83.
- Organic sulfur compounds.
  - *Ann.* 51 (1844), 303.
  - *Ann.* 87 (1853), 369.
  - *Ann.* 107 (1858), 234.
  - *Compt. rend.* 36 (1853), 1095.
  - *Compt. rend.* 46 (1858), 1280.
  - *Ann.* 126 (1863), 279.
  - *J. prakt. Chem.* (2) 14 (1876), 199.
  - *Ann.* 243 (1888), 204; 272 (1893), 276.
  - *Z. physiol. Chem.* 20 (1895), 269.
  - *Z. anorg. Chem.* 15 (1897), 14.
  - *Ber.* 31 (1898), 2283.
  - *J. Chem. Soc.* 77 (1900), 160; 91 (1907), 1394.
  - *J. prakt. Chem.* (2) 66 (1902), 423.
  - *J. Chem. Soc.* 101 (1912), 936; 103 (1913), 3.
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  - *Ann.* 83 (1852), 349; 199 (1875), 321.
  - *Ber.* 1 (1868), 171; 12 (1879), 2323.
  - *J. prakt. Chem.* (2) 39 (1889), 99.
  - *Ber.* 31 (1898), 2283; 38 (1905), 975.
  - *Ann.* 305 (1899), 191.
  - *J. Am. Chem. Soc.* 34 (1912), 292.
- Unsaturated amines.
  - *Ann.* 134 (1865), 11.
- Quarternary ammonium salts.
  - *Ann.* 78 (1851), 272; 107 (1858), 223; 108 (1858), 6.
  - *Ber.* 16 (1883), 2737; 31 (1898), 2283; 38 (1905), 2686.
  - *J. Chem. Soc.* 109 (1916), 1299.
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  - Fränkel, "Arzneimittelsynthese." 4th Ed., 1919, p. 670.
  - "Realenzyk. Pharm." VI 481.
  - *Ber.* 18 (1885), 1925; 19 (1886), 2585; 20 (1887), 1445, 2217.
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  - *Z. physiol. Chem.* 20 (1895), 288, 291.
  - *J. Chem. Soc.* 101 (1895), 1552.
  - *J. prakt. Chem.* (2) 55 (1897), 91.
  - *Ber.* 39 (1906), 3593.
- Urea.
  - *J. prakt. Chem.* (1) 35 (1845), 51.
  - *Compt. rend.* 21 (1845), 636.
  - *Ann.* 62 (1847), 78; 83 (1852), 339; 82 (1852), 311; 101 (1857), 321.
  - *Jahresber.* 1857, 364.
  - *J. prakt. Chem.* (2) 47 (1893), 567.
  - *Z. Chem.* (2) 4 (1868), 303.
  - *J. Chem. Soc.* 22 (1869), 12.
  - *Ann.* 150 (1869), 238.
  - *J. prakt. Chem.* (2) 30 (1884), 92.
  - *Ber.* 18 (1885), 461.
  - *Ann. chim. phys.* (6) 9 (1886), 300.
  - *J. prakt. Chem.* (2) 47 (1893), 567.
  - *J. Chem. Soc.* 63 (1893), 199.
  - *Gazz. chim. ital.* 27 I (1897), 1.
  - *Z. anal. Chem.* 39 (1900), 551.
  - *Ber.* 36 (1903), 1156.
  - *Z. anorg. Chem.* 49 (1906), 14.
  - *Am. Chem. J.* 47 (1912), 396.
- Cyanides.
  - *Ann.* 110 (1859), 202; 154 (1870), 121.
  - *J. prakt. Chem.* (2) 4 (1871), 38; (2) 6 (1872), 98.
  - *Ber.* 16 (1883), 2737.
  - *J. Chem. Soc.* 77 (1900), 163; 109 (1916), 1299.
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  - *Ann.* 62 (1847), 301; 80 (1851), 123; 82 (1852), 232; 85 (1853), 289; 101 (1857), 321; 119 (1861), 43.
  - *J. prakt. Chem.* (2) 3 (1871), 311; (2) 11 (1875), 317; (2) 20 (1879), 334.
  - *Compt. rend.* 78 (1874), 1707.
  - *Z. anal. Chem.* 22 (1883), 341.
- Nitrotoluenes.
  - *Gazz. chim. ital.* 36 I (1906), 229.
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  - *Gazz. chim. ital.* 36 I (1906), 229.
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  - *J. prakt. Chem.* (1) 36 (1845), 97.
  - *J. Chem. Soc.* 7 (1855), 75.
  - *Ber.* 16 (1883), 2737.
  - *Ann.* 224 (1884), 349.
  - *J. Chem. Soc.* 53 (1888), 555.
  - *Ber.* 21 (1888), 856, 1792.
  - *J. prakt. Chem.* (2) 39 (1889), 100.
  - *Monatsh.* 10 (1889), 899.
  - *Ann.* 260 (1890), 6.
  - *Gazz. chim. ital.* 23 II (1893), 525.
  - *Z. anorg. Chem.* 15 (1897), 208.
  - *J. Chem. Soc.* 101 (1895), 1556.
  - *Ber.* 31 (1898), 2293.
  - *J. Chem. Soc.* 79 (1901), 839.
  - *Z. anorg. Chem.* 46 (1905), 390; 57 (1908), 98.
  - *Ann.* 365 (1909), 50.
  - *Gazz. chim. ital.* 39 I (1909), 149.
- Benzonitrile.
  - *Ber.* 47 (1914), 1369.
- Pyrrole.
  - *Ann.* 105 (1858), 356.
- Piperidine.
  - *J. prakt. Chem.* (2) 39 (1889), 99; (2) 43 (1891), 159; (2) 47 (1893), 475; (2) 49 (1894), 401.
  - *Compt. rend.* 115 (1892), 880.
  - *Gazz. chim. ital.* 27 I (1897), 19.
  - *Z. anorg. Chem.* 15 (1897), 230.
  - *J. Chem. Soc.* 103 (1913), 6.
- Alkyl piperidines.
  - *Ber.* 18 (1885), 912; 33 (1900), 3515.
  - *J. Chem. Soc.* 103 (1913), 6.
- Pyridine.
  - *Ber.* 21 (1888), 1587.
  - *Ann.* 247 (1888), 5 ff.
  - *Monatsh.* 10 (1889), 892.
  - *Compt. rend.* 112 (1891).
  - *Gazz. chim. ital.* 25 II (1895), 423.
  - *Z. anorg. Chem.* 15 (1897), 228.
  - *Ber.* 37 (1904), 1260, 4610; 38 (1905), 975, 2003.
  - *Z. anorg. Chem.* 46 (1905), 367; 44 (1905), 8; 57 (1908), 101.
  - *Chem. Zentr.* 1910 II 1741.
  - *J. Chem. Soc.* 103 (1913), 6.
- Dipyridyl.
  - *J. Chem. Soc.* 22 (1869), 409.
  - *Ber.* 31 (1898), 2282.
  - *J. prakt. Chem.* (2) 84 (1911), 203.
- Methylpyridines.
  - *Ann.* 60 (1846), 99.
  - *Ber.* 18 (1885), 51, 3092, 3437.
  - *Bull. soc. chim.* (2) 43 (1885), 172.
  - *Ber.* 20 (1887), 812, 1660, 2732.
  - *Ann.* 247 (1888), 13.
  - *Ber.* 21 (1888), 293.
  - *Gazz. chim. ital.* 27 I (1897), 23.
  - *Z. anorg. Chem.* 15 (1897), 229.
  - *J. Chem. Soc.* 81 (1902), 452; 103 (1913), 3.
- Dimethylpyridines.
  - *Ann.* 80 (1851), 61; 231 (1885), 22.
  - *Ber.* 18 (1885), 51, 914, 3441; 20 (1887), 129.
  - *Ann.* 247 (1888), 30.
  - *Ber.* 21 (1888), 1008; 29 (1896), 2997; 32 (1899), 2528; 34 (1902), 3700.
  - *J. Chem. Soc.* 81 (1902), 452.
  - *Chem. Z.* 2 (1903), 414; *Chem. Zentr.* 1903 I 1034.
- Ethylpyridines.
  - *J. prakt. Chem.* (2) 43 (1891), 155.
  - *Ann.* 301 (1898), 152.
  - *Ber.* 31 (1898), 290.
- Methylethylpyridines.
  - *Ber.* 3 (1870), 262; 24 (1892), 3486.
- Trimethylpyridines.
  - *Ber.* 21 (1888), 1012, 2714; 25 (1892), 3487; 29 (1896), 2998.
  - *J. Chem. Soc.* 81 (1902), 455.
- Diethylpyridine.
  - *Ann.* 247 (1888), 49.
- Propylpyridine.
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- Allylpyridine.
  - *Ibid.* 28.
- Quinoline.
  - *Ann.* 42 (1842), 312; 44 (1842), 279.
  - *Ann. chim. phys.* (3) 9 (1843), 173.
  - *Ann.* 47 (1843), 83; 52 (1844), 139.
  - *Compt. rend.* 57 (1863), 837.
  - *Ann.* 131 (1864), 114; 247 (1888), 94.
  - *Monatsh.* 10 (1889), 892.
  - *Ber.* 23 (1890), 438.
  - *Gazz. chim. ital.* 25 I (1895), 399 ff.
  - *Ann.* 301 (1898), 133.
  - *Z. anorg. Chem.* 46 (1905), 365.
  - *Chem. Zentr.* 1910 II 1743.
  - *J. prakt. Chem.* (2) 84 (1911), 206.
- Miscellaneous nitrogen compounds.
  - *Ann.* 47 (1843), 64; 52 (1844), 13; 175 (1875), 43; 208 (1881), 137; 263 (1891), 274.
  - *Ber.* 15 (1882), 2106.
  - *Chem. Zentr.* 1913 II 1182.
- Aromatic ketones, thienyl ketones.
  - *Ann.* 267 (1892), 172.

- Alkaloids.
  - "Gmelin - Kraut - Friedheim - Peters Handbuch V," part II, 554.
  - *Ann.* 41 (1842), 118; 42 (1842), 315; 66 (1848), 268; 70 (1849), 73.
  - *J. Chem. Soc.* 1 (1849), 345.
  - *Ann.* 73 (1850), 372, 211; 74 (1850), 201; 77 (1851), 208.
  - *Phil. Mag.* (3) 37 (1851), 481.
  - *Ann.* 82 (1852), 311; 83 (1852), 339; 87 (1853), 8.
  - *J. prakt. Chem.* (1) 60 (1853), 239.
  - *Jahresber.* 1872, p. 270; 1873, p. 962.
  - *Ber.* 16 (1883), 2740.
- Aromatic sulfur compounds.
  - *Ann.* 243 (1888), 204.
  - *Ber.* 24 (1891), 757; 31 (1898), 2287.
  - *J. Chem. Soc.* 77 (1900), 164; 81 (1902), 1556; 91 (1907), 1395.
  - *Ber.* 47 (1914), 277.
- Aromatic tellurides.
  - *Ber.* 47 (1914), 278.
- Miscellaneous.
  - *Ann.* 229 (1885), 305; 233 (1886), 49.
  - *Ber.* 19 (1886), 700.
  - *J. Chem. Soc.* 49 (1886), 246.
  - *J. prakt. Chem.* (2) 39 (1889), 102; (2) 39 (1889), 99 ff.
  - *Monatsh.* 10 (1889), 891.
  - *Compt. rend.* 112 (1891), 995.
  - *J. prakt. Chem.* (2) 43 (1891), 155.
  - *Ann.* 267 (1892), 172.
  - *J. prakt. Chem.* (2) 47 (1893), 566.
  - *Ber.* 30 (1897), 2844.
  - *Gazz. chim. ital.* 28 II (1898), 113.
  - *J. prakt. Chem.* (2) 66 (1902), 423 ff.
  - *J. Chem. Soc.* 81 (1902), 1560.
  - *Ber.* 37 (1904), 3284.
  - *Chem. Zentr.* 1907 I 1103.
  - *J. Am. Chem. Soc.* 35 (1913), 951.
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1918.

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- *Ibid.* 484. Swed. Pat. 43,001.
- *Ibid.* 588. Can. Pat. 181,655, 181,656, 181,657.
- *Ibid.* 1050. Brit. Pat. 112,765, 112,766.
- *Ibid.* 1558. Norw. Pat. 28,538.
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1919

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- *Ibid.* 2040. U. S. Pat. 1,304,989.
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- *Ibid.* 2374. Swiss Pat. 78,339, 78,947.
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1920.

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- *Ibid.* 288. Brit. Pat. 132,557, 132,559.
- *Ibid.* 2040. U. S. Pat. 1,304,989.
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- *Ann. chimica* (4) 9 (1889), 258; (4) 10, 176; (1898), 16.
- *Ann. chim. phys.* (2) 39 (1828), 197; (7) 8 (1896), 268; (8) 14 (1908), 311.
- *Ann. farmacoterap.* (1898), 16.
- *Anz. Akad. Krakau* (A) (1910), 382.
- *Arch. Sci. Phys. Nat. Geneve* 6 (1898), 385.
- *Arch. farmacol.* 7 (1908), 94.
- *Arch. farm. sperim.* 11 (1911), 457.
- *Arch. Physiol.* 40 (1888), 533.
- *Atti accad. Lincei* (5) 1 (1892), 312, 431; (5) 2 I (1893), 423; (5) 5 (1896), 120; (5) 8 I (1899), 130; (5) 9 I (1900), 255; (5) 10 I (1901), 362, 413; (5) 11 II (1902), 65; (1903), 294; (5) 14 II (1905), 199; (5) 15 II (1906), 459; (5) 16 I (1907), 87; (5) 21 II (1912), 88, 640, 773.
- *Ber.* 6 (1873), 440; 15 (1882), 830.
- *Ber. Berl. Akad.* (1866), 586.
- *Ber. Wien. Akad.* 9 (1852), 252; (II) 86 (1882), 1158; (II) 99 (1890), 173.
- *Biochem. Z.* 11 (1908), 294; 24 (1910), 173,423; 25 (1910), 341; 32 (1911), 59, 511; 33 (1911), 381; 35 (1911), 505; 36 (1911), 291; 37 (1911), 142; 39

(1912), 50; 40 (1912), 498; 57 (1913), 260; 65 (1914), 460.

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Bull, acad. Belg. (3) 33 (1897), 821; (1903), 441.

Bull. soc. chim. (2) 14 (1870), 217.

Chem. Zentr. 1902 I 500; 1907 I 483; 1915 II 565, 569, 1260.

Chem. Abst. 6 (1912), 2262.

Chem. News. 19 (1869), 28.

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Compt. rend. 82 (1876), 1504; 112 (1891), 340, 995; 117 (1893), 44, 284, 518; 119 (1894), 559; 120 (1895), 628, 781, 850; 121 (1896), 253; 126 (1898), 1043, 1145, 1277, 1868; 127 (1898), 963; 128 (1898), 429; 129 (1899), 113, 379, 918; 130 (1900), 837, 1256, 1478, 1511; 131 (1900), 346; 132 (1901), 145, 635; 137 (1903), 255, 714; 140 (1905), 1698, 1703; 142 (1906), 1200; 144 (1907), 326, 1177; 146 (1908), 754; 152 (1910), 1867; 153 (1911), 304, 1520.

Compt. rend. soc. biol. 69 (1910), 508; 74 (1913), 18.

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J. prakt. Chem. 86 (1862), 298; (2) 13 (1876), 437; (2) 55 (1897), 88.

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Phil. Mag. (3) 13 (1838), 431; Aug. 1847; (4) 20, 111; (5) 2 (1876), 277.

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Z. Chemotherapie, 1 (1912), 21.

Z. Krystallog. 51 (1912), 138.

Z. ges. Schiess-Sprengstoff. 6 (1911), 4 ff.

Z. Hyg. Infekt. 25 (1897), 1; 66 (1910), 497; 70 (1911), 24; 82 (1916), 279.

Z. Immunität. (I) 1 (1908), 108; (I) 16 (1913), 224; (I) 20 (1914), 378; 41 (1915), 47.

Z. physiol. Chem. 15 (1890), 1; 20 (1895), 267, 288; 22 (1896), 520; 23 (1897), 505; 36 (1902), 401; 43 (1904), 350; 44 (1905), 503; 47 (1906), 173; 55 (1908), 352; 57 (1908), 49; 78 (1912), 333; 83 (1913), 249.

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Z. Zuckerei 62 (1912), 318.

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APPENDIX E.

Patents on Organic Mercury Compounds.

German Patents.

Abbreviations. C. = Chemisches Zentralblatt.
C. A. = Chemical Abstracts.
Fr. = Fränkel, Die Arzneimittelsynthese. 4th Ed. 1919.
Frdl. = Friedländer, Fortschritte der Teerfarbenfabrikation.
G. K. F. P. = Gmelin-Kraut-Friedheim-Peters, Handbuch der anorg. Chemie, Vol. V, Part II.

48,459.	Fr. 659.
104,904.	Fr. 674. Frdl. V 724.
118,050.	G. K. F. P. 516.
121,656.	Fr. 674. Frdl. V 724.
125,095.	G. K. F. P. 968.
125,392.	G. K. F. P. 459.
132,660.	Frdl. VI 1102.
137,560.	C. 1911 I 695.
143,448.	C. 1903 II 403. Frdl. VII 715. Fr. 661.
143,726.	C. 1903 II 474. *Ber.* 31 (1898), 2154. *J. prakt. Chem.* (2) 89 (1914), 136. Frdl. VII 716. Fr. 662.
148,794.	(1902), Raupenstrauch.
157,663.	Fr. 674.
171,485.	C. 1906 II 385. Frdl. VIII 1231.
182,217.	(1905), Reissert.
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